

**DEVELOPMENT OF B<sub>4</sub>C AND MoS<sub>2</sub> NANOCOATINGS  
ON CUTTING TOOLS**

By

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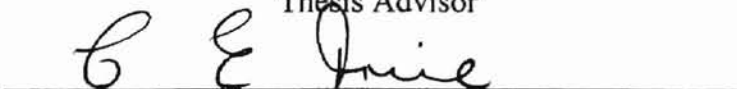
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## PREFACE

This study dealt with the development of the multiple nanocoatings of hard and lubricating materials on WC- 6% Co cutting tools. Pulsed laser deposition method was employed to deposit boron carbide ( $B_4C$ ) and molybdenum di sulfide ( $MoS_2$ ) nanocoatings using a 193 nm wavelength Excimer laser.  $B_4C$  was chosen as the hard material because of its high hardness (9.3 Mohs or 3200 Knoop  $Kg/mm^2$  at room temperature). But, it is well known that this material oxidizes rapidly at temperature greater than  $1100^\circ C$  forming  $B_2O_3$ [1].  $B_4C$  has high wear resistance, chemical resistance and high strength to weight ratio.  $MoS_2$  is a soft, solid lubricating material (the coefficient of friction is 0.01 to 0.1). Thus, it can increase the efficiency in dry machining by providing the lubrication action in conventional machining practice.

In this investigation a Lambda Physik ArF excimer laser (193 nm wavelength) and 10 Hz repetition rate was used for pulse laser deposition of alternate nanolayers of  $B_4C$  and  $MoS_2$  on a cemented tungsten carbide substrate. The substrate temperature was raised to  $600-700^\circ C$  during the coating deposition of  $B_4C$ . During the deposition of  $MoS_2$  the substrate temperature was raised to  $400^\circ C$ . The deposition chamber pressure was maintained at  $5 \times 10^{-5}$  Torr.

The cemented carbide substrates were polished by diamond paste, cleaned ultrasonically, etched with Murakami's reagent prior to coating. The surface of the substrates was also cleaned by the laser beam prior to and during the film deposition.



In an effort to increase the deposition rate, a magnetic field was employed outside the chamber, just above the imaginary line connecting the substrate and the target. Magnetic field directs the charged particles of the plume towards the substrate. It also filters out the heavy particles. After applying the magnetic field, the film growth rate was found to increase. The film deposition rate was also found to increase with the increase in the magnetic field intensity.

The coated substrates were examined with an optical microscope, microXam laser interference microscope and Zygo laser interference microscope. Adhesion was tested scribing with a SiC (hardness 9.2 Mohs or 2500 Knoop kg/mm<sup>2</sup>) tipped chisel, while observing the surface under optical microscope and the microXam. It was found that the coatings did not peel off when scribed by chisel. But, the scribing mark could be seen under the optical microscope and microXam. The coatings developed at the substrate temperature of 600-700°C were found to be better than those obtained at 400°C. But, the coatings were found to be softer than the WC substrate. In order to get good adhesion of the deposited film, the substrate temperature should be raised further (800-1000°C) or a suitable buffer layer should be used in between the substrate and the B<sub>4</sub>C coatings.

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## Chapter I

### INTRODUCTION

The demands for hard, tough and environment friendly cutting tools are increasing due to the changed social and economic circumstances. So, a large number of manufacturing industries are moving towards some non-conventional ways of manufacturing. Dry machining is a major road in this regard. It does not have the advantages of a cutting fluid, so alternatives are needed to give the same result. Coatings on cutting tools are one approach to address this problem. Multi-layer nanocoatings can provide more fracture toughness than that of bulk material. As it has more wear resistance, the tool efficiency can also increase. A proper selection of hard/lubricant coatings can give the cutting tools the required hardness, toughness and self-lubrication. Alternate layers of multi-layer nano-coating of  $B_4C$  and  $MoS_2$  is a good pair to perform this function.

Boron carbide ( $B_4C$ ) is a stable, refractory material of high hardness. Its density is low. It possesses high wear resistance, chemical resistance, high melting temperature, high modulus of elasticity, and high strength to weight ratio [1]. So, it is a good choice as a material for tool coatings. A  $B_4C$  nano-coating gives the cutting tool increased hardness and wear resistance. A  $MoS_2$  nano-coating gives lubrication during the cutting process. Alternate layers of  $B_4C$  and  $MoS_2$  give the advantages of both the materials.

Pulse laser deposition (PLD) is a physical vapor deposition (PVD) process. It has some advantages over other coating processes as will outlined on the followings and it is a popular choice in nano-coating, semi-conductor manufacturing, super-conductive material growth and nano-crystal growth.

### Pulse laser deposition

Pulsed laser deposition (PLD) can be characterized as a flash evaporation method. A powerful laser beam strikes the target material, heat energy is absorbed and a thin surface region is vaporized. Thus, it produces a condensible vapor and creates a conical plume of evaporant, which extends along the direction normal to the target surface. The plume consists of both ionized and neutral species. The coating grows on the cutting tool, as the plume deposits on the substrate. Species present in the plume typically have energy in the range of 10 -100 eV [2]. So, they do not require high temperatures to supply energy during surface interactions with the substrate. To reduce collisions between random atoms in the chamber and the species in the plume, the chamber is kept in vacuum. The vacuum also prevents contamination during coating growth.

PLD is very useful technique for preparing a wide range of thin films and multi-layer structures. This process is cost effective, simple, and easy to use. It produces products of good quality. The product quality can be comparable to that of molecular beam epitaxy (MBE), which is a very costly technique. Another advantage of PLD is that the energy source is independent of the film deposition system.

The PLD system has few components. Figure 1 shows the essential parts of a PLD system. The components are laser, vacuum chamber, target, target holder, substrate,

vacuum pump, substrate heater, thermocouple and pressure gauge. The thermocouple measures the tool temperature and the pressure gauge measures the pressure in the vacuum chamber. There is a viewing window, which allows observation of the optical path and enable adjustment it, if required. An energy meter measures the energy of the incident laser beam. The target is rotated by a motor so that the top surface of the tool can be vaporized uniformly. An electrical resistance heater is placed adjacent to the substrate to heat the tool substrate to the desired substrate temperature. Figure 2 shows the deposition chamber and adjacent equipment.

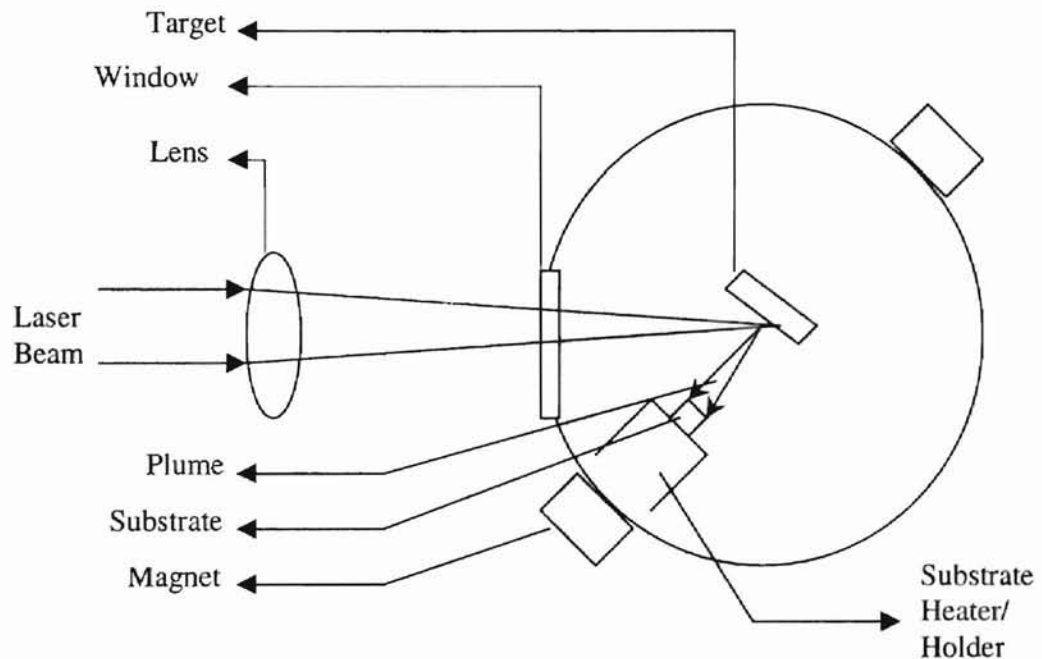


Figure 1: Schematic diagram of the experimental setup  
(Top view)

There are two problems associated with the pulsed laser deposition (PLD) system. They are splashing and lack of uniformity of the film developed over a large area. The lack of uniformity is due to a narrow angular distribution of the plume. The reasons for splashing are mainly sub-surface boiling, expulsion of a liquid layer by shock wave, and exfoliation. The sub-surface boiling (also called true splashing) occurs when the subsurface layer gets superheated before the surface layer. It can happen if the time to transfer the laser energy into heat energy is shorter than the time needed to evaporate the surface layer. This phenomenon produces a micron-sized molten globule onto the substrate. Any material can have this problem, especially a material with a low melting and boiling point. The rate of splashing decreases with decreasing laser power, but results in a decrease in the deposition rate [3].

The force for the expulsion of the liquid droplets comes from the recoil pressure exerted by the shock wave of the plume. The force starts above the liquid layer. This phenomenon also produces micron-sized condensed globules, like true splashing. Lowering the laser power and, subsequently, causing the lowering of deposition rate can lower it. In the exfoliation process, random shaped solid particulate material ejects from the target. The particulate size and the ejection rate depend on the surface morphology and the laser power density. It can happen to most materials but is common to sintered ceramic targets. The high power repetitive laser beam erodes the surface and forms long needle shaped microstructures of a few microns in dimension. These needles direct toward the oncoming laser beam. They are very fragile and can be broken by thermal shock associated with the intense laser irradiation. The rapidly expanding plume carries loose debris that condenses on the film [3].



There are several methods available to eliminate or reduce the splashing problem. One method utilizes a mechanical velocity selector, which is placed between the target and the substrate, it allows high velocity particles and removes slow moving particles. Another technique is plume manipulation. In which the substrate is placed at the intersection of the axes of two plumes behind a collimator. The collimator is used to skim the scattered species. Because of its intricacy, this technique is not used much. A widely used technique is target surface modification. High density and smooth surfaces are the properties of a target that minimize splashing. Some researchers heat the targets close to the melting point of the target, so that the surface remains smooth after continuous laser radiation. But, in this approach, the vapor pressure of the target material should be low, as it does not produce sufficient evaporation rate [3].

### Structure of boron carbide

Boron carbide has a complex crystal structure based on  $B_{12}$  icosahedra and three atom linear chain building blocks. It is stoichiometrically  $B_4C$ . But, the boron to carbon ratio can vary over a wide range by the partial substitution of boron by carbon atoms both in the chain and in the icosahedra [4]

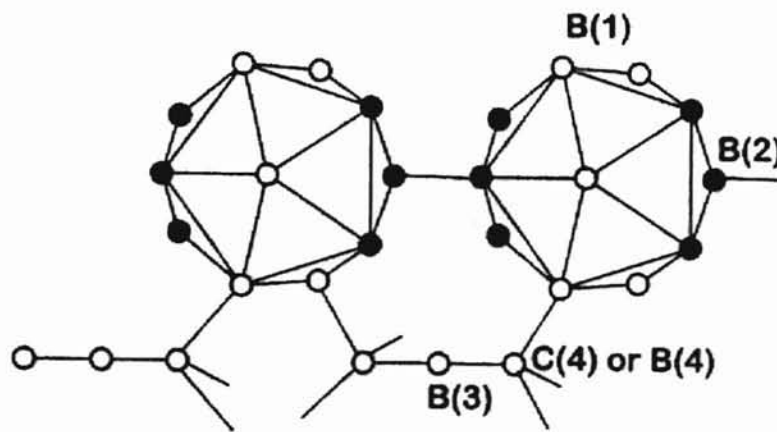


Figure 2: Structure of Boron carbide [4].

### Structure of molybdenum di-sulfide

The crystal structure of  $\text{MoS}_2$ , used, as lubrication material, is hexagonal. But, it can have other structures, such as trigonal. Even, complex structure, such as buckyballs can be formed from it [5]. Commonly, the known chemical formula is  $\text{S}=\text{Mo}=\text{S}$ . Mo has 6 coordinates and S has 3 coordinates. In to Figure 3, black and white balls represent Mo and S, respectively.

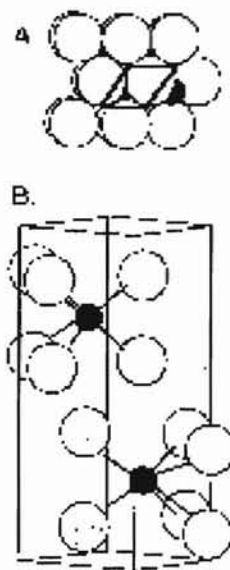


Figure 3: Crystal Structure of hexagonal  $\text{MoS}_2$  [6].

## Chapter II

### BACKGROUND AND LITERATURE REVIEW

The invention of the ruby laser enabled researchers to study the interaction between an intense laser beam and solid surfaces. During this time, it was suggested that thin films could be deposited by laser radiation [3,7,8]. Unfortunately, limited work was done in this area due to a lack of technological advantages.

In the mid-1970s, the electronic Q-switch was developed. The advantage of this system is that it becomes possible to deliver short pulses with a very high peak power intensity. The PLD technique was focused to be a good tool for film growth during the 1980s [3,8]. Numerous works to date from this time are reported in reference 3.

In the following, the following topics will be briefly reviewed: hard coatings, solid lubricant coatings, multi-layer coatings, target condition, chamber environment, substrate heat treatment, films orientation and films of electrical and magnetic interest.

#### Hard coatings

Laidani et al [9] developed and studied B-C-N films produced by the PLD technique. They used a B<sub>4</sub>C target in a N<sub>2</sub> atmosphere. The substrate was Si (100). A KrF excimer laser of 248 nm wavelength and 20 ns pulse duration was used. The Si substrate

was cleaned in a 10% HF solution to remove any oxide layer. The target to substrate distance was kept at 45 mm. The chamber was initially evacuated to a pressure  $2.5 \times 10^{-5}$  Pa. Nitrogen gas was introduced and the pressure was set to 5 Pa. The coated films developed were reported to be without voids or corrugations and were adhesive. The ratio of boron and nitrogen was also reported to be uniform. Some oxygen was also found in the films. They found the chemical bonds of the film to be B-N, C-C and C-N. They did not find any B-C bond in the film. In this research, the deposited films were claimed to be well adherent to the substrates. But, they did not quantify the term's well adhesive, hardness, coefficient of friction and Young's modulus of the deposited films. From the foregoing, it would seem that nitrogen atmosphere in the chamber help to get adherent and uniform film. It also plays an important role in the chemical structure of the deposited  $B_4C$  coatings. However, they did not report any affect of the nitrogen pressure on the deposited coatings.

Oliveira et al [1] deposited boron carbide on fused silica plates by laser assisted chemical vapor deposition (LCVD) process. They used a gas mixture of  $BCl_3$ ,  $CH_4$ ,  $H_2$  and Ar at a working pressure of 133 m bar and normal pressure. They also used continuous mode  $CO_2$  laser. They found that a dark color of the coated area corresponds to more than 40% of free carbon. A gray and shiny surface area was by rhombohedral boron carbide. In this research, they found that at normal pressure, the crystal morphology was the same as found at 133 m bar pressure. But the grain size of the film was smaller at normal pressure. They anticipated this, caused by lower substrate surface temperature due to high absorption of heat by gases at normal pressure. But, they did not report the temperature of the substrate surface. They found the presence of some SiC in

XRD analysis but could not find it in micro-Raman spectroscopy analysis. They also anticipated that the SiC was formed at the interface between the substrate and the film. But, they did not explain, why it was not formed in the film. From the above research, it would seem that the pressure of gases in the deposition chamber play an important role on the grain size of the films.

Eckardt et al [10] developed a B<sub>4</sub>C boron carbide coating (with Ti interlayer) by a d.c. magnetron sputtering process. A B<sub>4</sub>C target (99.5% purity and 20.9% carbon) was used. The pressure in the chamber was maintained 10<sup>-3</sup> Pa. Ball bearing steel, high speed steel, silicon were used as substrate materials. The substrate temperature used was low and not more than 200°C. The B<sub>4</sub>C was deposited on silicon substrate with an interlayer of titanium. The process involves evacuation of the chamber, argon ion etching, titanium deposition and sputtering of boron carbide. The coefficient of friction was studied by a pin-on-disc tester. The best coefficient of friction found to be 0.2 when the coating was deposited in the presence of a small amount of acetylene. The best hardness and elastic modulus found were 41 GPa and 283 GPa, respectively. The hardness obtained was higher than that obtained for pure B<sub>4</sub>C. They anticipated that the lower coefficient of friction was caused by the occupation of H in the voids and the higher hardness was because of a structural change caused by the introduction of additional bonds of B-H and C-H. However, they could not give any evidence in support of their hypothesis. Seemingly, the titanium interlayer facilitates good adherent coatings of B<sub>4</sub>C on the above mentioned substrates. Probably, the thermal expansion coefficient of the interlayer plays an important role for this good adhesion. Another reason might be the high chemical reactive nature of the Ti.

Capano et al [11] deposited TiCN thin films by the PLD method, ablating pure TiC targets with a laser of 248 nm wavelength and in a nitrogen atmosphere in the chamber. The substrate was 440C stainless steel. The nitrogen gas pressure was 0.6 Pa or 2.6 Pa. At 673 K temperature, the TiC target was ablated at a pressure of  $7 \times 10^{-7}$  Pa for 30 minutes. The nominal thickness of all films grown was found to be 800 nm. By X-ray Photoelectron Spectroscopy (XPS) spectra analysis, they found that nitrogen was incorporated into the films. They also found oxides in the films. This contamination was due to the porous nature of the target, which contained oxygen. For hardness tests (nano-indentation), they found that for higher nitrogen concentrations the hardness of TiCN was similar to TiN (about 24 GPa), but, for lower nitrogen (film containing 17% nitrogen) concentrations, the hardness was 60 GPa. At a nitrogen concentration of 37.9% in the film, the hardness was found to be only 23 GPa. In this research, the phenomenon of lowering of nitrogen concentration in the deposition chamber, causing higher hardness of films was not explained. The conclusion is that an optimum nitrogen pressure helps to deposit a hard coating of TiCN.

Craciun et al [12] deposited a thin TiN film on glass and silicon substrates by reactive PLD method. A KrF excimer laser of wavelength 248 nm was used to ablate a pure metallic Ti target in a nitrogen atmosphere. The substrate temperature was 400 °C and the nitrogen pressure was  $6 \times 10^{-4}$  Torr. The target to substrate distance was 4 cm. They developed continuous polycrystalline films of FCC TiN under optimum conditions. The surface was smooth and the film had good chemical and wear resistance. But, the researchers did not quantify the wear resistance capability of the films. As their main interest was optical properties, they repeated the same optical tests after exposing six

months to air and claimed the films had the above properties. From the foregoing, it would seem that an optimum substrate temperature, the target to substrate distance, atmosphere and the pressure of the chamber are required to get good optical properties of the deposited films.

Kumar et al [13] deposited a TiC coating on a Si (100) substrate by the PLD method. The pressure in the chamber was  $10^{-8}$  Torr. The substrate temperatures were room temperature, 300°C, 500°C and 650°C. The Young's modulus was obtained from nano-indentation. They found that the film structure was strongly dependent on the substrate temperature. At room temperature, the film's quality and adhesion was reported to be not satisfactory. At 600°C, the film structure was found to be crystalline. At this temperature, it showed the highest hardness and Young's modulus values of 25 GPa and 239 GPa, respectively. In this research, they did not show reasons behind the temperature (substrate) dependence of the hardness and Young's modulus of the films. The conclusion is that the substrate temperature during the coating deposition, is the most important factor for adhesion and strength of the films.

Obata et al [14] grew TiN films on a Si (100) substrate by the PLD technique. The TiN target used was 99.5% pure, hot pressed TiN. The substrate was cleaned by 10% HF acid solution. A KrF excimer laser of 248 nm wavelength, 34 ns pulse duration and repetition rate of 5 Hz produced a homogeneous beam. The chamber pressure was  $5 \times 10^{-7}$  Torr. The substrate temperature during growth was 700°C. On each sample, a 170 nm film was grown. The homogeneous laser beam decreased the number of particles in the film as compared to that of a non-homogeneous laser beam. The reasons for the dependence of surface roughness and the number of particles in the film, on the beam



type were not investigated. From the above research, it can be concluded that the homogeneous nature of the laser beam is a very important factor for the surface roughness and the formation of particles in the films.

Wang et al [15] studied the growth of AlN and GaN on a sapphire substrate by the PLD method. They investigated the effect of substrate temperature and ambient pressure on the structure and found an amorphous film when the temperature and pressure were low. They grew cubic AlN at a temperature of 800°C and 0.2 Torr and GaN at 600°C, with a buffer layer of cubic AlN. The chamber pressure was  $10^{-5}$  Torr. An ArF excimer laser of 193 nm wavelength was used with a pulse repetition rate of 10. X-ray Diffraction (XRD) and Raman spectra analysis showed that the GaN thin film, without a buffer layer of AlN, consisted of a mixture of hexagonal and cubic GaN structures. When an AlN buffer layers was used, the structure contained mainly cubic GaN. Mechanical and electrical properties of the film were not investigated. From the foregoing, it would seem that a buffer layer of AlN plays an important role on the crystal structure of the GaN films. Probably AlN played the role of seed in the formation of GaN films.

Santerre et al [16] studied the properties of TiC thin films grown by the PLD method. A polycrystalline TiC target was used. The substrates were Si (100) and fused silica. The substrate temperature ranged from 25 to 600°C. A KrF excimer laser of wavelength 248 nm, pulse width 12 ns, and repetition rate of 30 Hz was used. The target was made of hot pressed TiC powder with no binder. Chamber pressure was  $1 \times 10^{-5}$  Torr. The substrate to target distance was 6.5 cm. Polycrystalline TiC thin films developed on both the targets. All the films showed a (111) orientation. They found that some oxygen atoms were incorporated in the film substituting for some carbon atoms. The compressive

strength of the film was in the range of -7 to -3 GPa. They found an increase of compressive strength of the film with the substrate temperature. They could not make the deposited film particulate free. The conclusion is that the substrate temperature influences the strength of the deposited films. But, the films orientation is independent of the substrate temperature.

Donley et al [17] synthesized TiC and B<sub>4</sub>C thin films by the PLD method. The substrates were kept at room temperature and at 300°C. A KrF excimer laser of 248 nm wavelength, a pulse repetition rate of 100 Hz, and 15 ns pulse duration was used. The chamber pressure was kept  $9 \times 10^{-7}$  Pa during film growth. The laser beam power was 230 mJ. The distance between substrate and target was 5 cm. The substrate temperature was measured by a pre-calibrated infrared pyrometer. A calibrated quartz crystal was used to measure film thickness and deposition rate. Prior to deposition, the targets were cleaned by rinsing with acetone and methanol before loading into the chamber. TiC films were grown on a polished 440C stainless steel substrate. The B<sub>4</sub>C thin films were developed on a Si (100) substrate. Native oxide layers were not removed. A ball on disc apparatus was used to investigate the tribological properties of the films. A 3.175 mm diameter sapphire ball with 100 gm load was used. The disc was rotated at 100 rpm. X-ray Photoelectron Spectroscopy (XPS) was used to analyze the films of TiC and the target. Very little difference was found between them. Using Raman spectroscopy, they confirmed that there was no appreciable amount of oxides in the coating. The coefficient of friction of TiC was 0.2 at an early stage of the tests, when the coating thickness was 200 nm. After that, there was abrasive wear of the steel ball and the film started to fail after 400 revolutions. Following it, the coefficient of friction increased to 0.8. For the B<sub>4</sub>C coating,

the ratio of carbide to graphite was found to be 3. This ratio changed to 1/3 after 20 minutes of sputtering. The film was seen to be uniform and non-porous, by SEM. The coefficient of friction of the film of 200 nm was found to be 0.5. The film failed after 200 revolutions. This was attributed due to the presence of the native oxide layer. In the B<sub>4</sub>C coating, they could not avoid the presence of graphite in the films. From the foregoing, it would seem that the lack of adhesion of the film to the substrate was the main problem, the researchers could not solve. And even in low chamber pressure there was enough oxygen, which caused the presence of oxygen in the deposited coatings. Probably this problem can be avoided by putting inert gas with a low partial pressure in the deposition chamber.

Shim et al [18] studied the fabrication of diamond-like carbon (DLC) thin films by the PLD method. A Nd: YAG laser with wavelength of 355 nm and frequency of 5 Hz was used with a Si (100) substrate. The substrate was ultrasonically degreased with acetone and methanol for 3 minutes. The substrate temperature was varied from room temperature to 600°C. They claimed to have obtained good quality DLC films at 300°C, laser fluence of 12 J/cm<sup>2</sup>. But, they did not measure mechanical or electrical properties of the deposited films. Other problems with this research, were the presence of graphite and diamond particles. The conclusion is that optimum substrate temperature and laser fluence are required for good quality films. This conclusion is similar to Kumar [13] and Obata [14].

Derkach et al [19] studied the plasma produced by laser irradiation of a boron carbide target. A XeCl excimer laser of a 308 nm wavelength and pulse repetition rate of 10 Hz was used. For a smoother film surface, a computer controlled substrate holder was

used which could move relative to the plume. They found different intensity profiles of the emitting species of boron and carbon. They also found that emission of the carbon transition lasted longer than that of the boron transition. The temporal variation of the plasma electron temperature and density were insignificant. They did not investigate the ablation dynamics of different species from the target. The conclusion is the different species of the plume possess different intensity profile. And the accuracy of their results depends on some assumptions.

Pelt [2] attempted to grow a SiC film on Si (100) substrate by the hybrid PLD/CVD technique. The objective of the hybrid technique was to ablate SiC target and at the same time supplying carbon through the dissociation of carbon-containing gas. CBr<sub>4</sub> was selected to supply carbon. CBr<sub>4</sub> has a low dissociation temperature of approximately 100°C. The substrate was cleaned with 1,1,1 trichloroethane for 5 minutes, then ultrasonically cleaned with acetone and methanol for 5 minutes each. Contaminants were removed by etching with a solution of de-ionized water, H<sub>2</sub>O<sub>2</sub> and HCl for 5 minutes. The final etching was carried with a 20:1 solution of de-ionized water and HF (49%). For PLD growth the substrate temperature was kept at 500°C and 700°C. A KrF excimer laser with a 248 nm wavelength was used. The target to substrate distance was 5.15 cm. The ultimate base pressure was 10<sup>-8</sup> Torr. Then, a canister introduced CBr<sub>4</sub>. The CBr<sub>4</sub> was heated and delivered to the chamber. The residual bromine was removed by an ion pump. The researcher found that successful growth of polycrystalline SiC was mainly dependent on the fluence of the laser. A high quality SiC film was grown at 700°C and a 5.15 cm target-substrate separation distance. In this research, the optimum target to substrate spacing was not investigated for the best quality of films. All growth parameters

were not optimized to deposit single-crystal SiC. It appears that laser fluence plays an important role for the deposition of SiC thin films. This conclusion is similar to Shim [18]. At the same time PLD/CVD hybrid method provides some advantages over the CVD method.

Ashino et al [20] studied a non-stoichiometric  $\text{TiO}_2$  (110) surface by noncontact AFM. The experiments were carried out under ultra high vacuum condition. The base pressure of the system was in the range of  $10^{-11}$  Torr. A specially designed scanning probe microscope was used, which could be used as a Scanning Tunneling Microscope (STM) and a non-contact Atomic Force Microscope (NC-AFM). They observed the atomic scale structures of reconstructed phases of oxygen-deficient  $\text{TiO}_2$ . They did not give the mechanical properties of the deposited films, as contact mode operation of AFM was not done.

Tsui and Redman [21] developed a substrate cleaning technique to improve the adhesion of diamond-like carbon coatings (DLC) to metal substrate in the PLD method. The pressure of the chamber was  $2 \times 10^{-3}$  Torr. A Nd: YAG laser of wavelength 1064 nm and repetition rate of 10 Hz was used to ablate the target materials. The substrate samples were rotated in order to get a smooth surface. A typical deposition rate under these conditions was found to be  $0.5 \mu\text{m/h}$  over a  $50 \text{ cm}^2$  area. Substrates were composed of 99% pure Ti, 440C stainless steel, and a cobalt alloy, Stellite 6b. Each substrate surface was polished to a fraction of a micron finish using  $0.2 \mu\text{m}$  diamond paste. Then, the substrate was cleaned ultrasonically with isopropyl alcohol bath for 30 minutes. After this, it was heated to about  $70^\circ\text{C}$  for 15 minutes. Then, the substrate surface was cleaned by a laser beam inside the chamber prior to the deposition of the coatings. The substrate

was removed from the chamber when the coating thickness was about 2  $\mu\text{m}$ . The coated surface was sandblasted with a jet of compressed air (at 40 psi pressure) carrying glass beads of 30-60  $\mu\text{m}$  in diameter. After sandblasting, the surface was observed under the optical microscope and the surface damage was assessed. When a 2  $\mu\text{m}$  DLC coated samples was sandblasted for 50 sec, about 50% of the DLC coating was removed from the surface. In similar experiments, researchers got a hardness of the DLC coating of 80 GPa and a coefficient of friction, 0.1. From these studies they reported that laser ablation cleaning process is expected to drive out absorbed gas and removes surface contaminants from the substrate surface. In this research, no effect was made for the laser scanning of the substrate surface prior to the deposition of the films. The surface temperature was estimated as 4000°C for both the substrates when exposed to 5 J/cm<sup>2</sup> laser energy density. This temperature should evaporate few monolayers of the substrate. It was assumed that at this temperature surface contaminants and gases would evaporate. The conclusion is that a systematic cleaning of substrate helps to make better adhesion. And sandblasting is a good technique to check the wear resistance property of the coatings.

#### Solid lubricant coatings

Zabinski et al [22] grew a zinc oxide film by the PLD method to serve as a high temperature lubricant. A KrF excimer laser of 248 nm was used. The base pressure of the vacuum chamber was  $9 \times 10^{-7}$  Pa. A 440°C stainless steel coupon was used as the substrate. The target was a commercially available ZnO disc of 99.9 % purity. The substrate temperature was either at 300°C or room temperature. To measure the film thickness, a calibrated crystal oscillator was used. Raman spectroscopy (SPEX 1877 spectrometer)

using an incident laser beam of 514.5 nm wavelength was employed to study bulk chemistry and film crystallinity. A ball-on flat tribometer was used to investigate the friction and wear properties. The coefficient of friction of polished ZnO (stoichiometric, hexagonal) is 0.65. But, on the grown film, the highest coefficients of friction achieved were 0.6 (transient condition) and 0.34 (steady state condition after 10000 cycles), when the substrate was kept at room temperature. At a substrate temperature of 300°C, the coefficient of friction obtained was 0.2. But, when the contact stress of ball was reduced from 675 MPa to 425 MPa by increasing the ball diameter to 6.75 mm, the coefficient of friction was found to be over 0.7. This was a very high coefficient of friction for a lubricating material. In the case of oxygen deficient nano-phase/nano-structured ZnO, the coefficient of friction was less than 0.2. For MoS<sub>2</sub>, the coefficient of friction lies between 0.1 to 0.01. From the foregoing, conclusion can be drawn that selecting ZnO as a lubricating material, other than working at a high operating temperature would not be a good choice. Another conclusion is that the coefficient of friction of ZnO coatings is dependent on the substrate temperature.

Prasad and Zabinski [23] described the room temperature tribological characteristics of nanocrystalline zinc oxide (ZnO) films. The films were grown on a 440C stainless steel substrate by the PLD technique. A hot pressed hexagonal ZnO target was used. The wavelength of the laser beam was 248 nm and pulse repetition rate was 10Hz. During coating development, the chamber pressure was  $6 \times 10^{-5}$  Pa. The pressure was maintained  $4 \times 10^{-3}$  Pa when oxygen was introduced into the system. In one set of experiments, the substrate was at room temperature with a base pressure of  $9 \times 10^{-7}$  Pa. In a second set of experiments, the temperature of the substrate was 300 °C and the chamber



pressure was  $9 \times 10^{-7}$  Pa. In the third set, oxygen with a partial pressure of  $4 \times 10^{-3}$  Pa was introduced in the chamber, while the substrate was at room temperature. In the final set, oxygen was maintained at the same partial pressure, while the substrate temperature was raised to 300 °C. A nano-indenter with a three-sided diamond pyramid was used to conduct hardness tests. The highest hardness they found was 11.92 GPa with a standard deviation of 5.8 GPa for a ZnO film at 300°C in vacuum. The SEM test revealed smooth surfaces without any grain boundaries. They found the coefficient of friction to vary from 0.16 to 0.34. But, for hot pressed ZnO disc, it was 0.65. The friction coefficient of ZnO film was observed to be sensitive to stress and sliding speed. They, also, found extensive plastic deformation of the ZnO film. As a high temperature lubricant, it might work well if a low coefficient of friction could be achieved. The conclusion is that for low temperature application, its use might not be economical. The researchers could not show reasons other than testing conditions for the variation of coefficient friction of the deposited coatings. Probably, parameters related to the coating growth process have influence on it. One of this parameter is the substrate temperature, as concluded by Zabinski et al [22].

Okoshi et al [24] deposited a ZnO film by the PLD technique. They used a mode locked Ti: sapphire laser of 790 nm and 10 Hz repetition rate. ZnO targets were used at a distance of 20 mm from Si (100) substrate. The chamber pressure was  $8 \times 10^{-4}$  Pa and the substrate temperature was 270°C. Crystallinity of the film deposited improved when the substrate temperature was raised above 150°C. They did not investigate the mechanical properties of ZnO. The conclusion is that the crystal structure of the deposited coatings depends on the substrate temperature.



Fox et al [25] deposited  $\text{MoS}_2$  and  $\text{MoS}_2/\text{Ti}$  composite coatings by closed field unbalanced magnetron sputtering. In this study, the coefficient of friction was found to be 0.2 and 0.6. On a scratch test, they did not get good adhesion.

#### Multi-layers coatings

Reeber et al [26] developed thin films of boron nitride/boron carbide composites (about 70% boron nitride). The film was 75 nm thick. After nitrogen ions were implanted, XeCl laser annealing followed. During the annealing, 50% of the nitrogen atoms got back to the hot surface. The temperature during nitrogen implantation was less than  $200^\circ\text{C}$ . Hexagonal boron nitride is a soft, lubricious, high temperature-stable solid. The laser annealing improved the fracture strength of the coating. In this research, the mechanical properties of the films were not investigated. The conclusion is that laser annealing can improve the fracture strength of the coatings. And nitrogen ion implantation is a good technique to grow multi-layers coatings with a nitrogen compound.

Ren et al [27] deposited boron-carbon-nitrogen thin films by laser ablation of boron carbide ( $\text{B}_4\text{C}$ ) under nitrogen ion bombardment. A YAG 532 nm laser beam with energy 30 mJ/pulse and repetition rate of 10 Hz was used. An external motor rotated the  $\text{B}_4\text{C}$  target. A nitrogen ion beam with energy in the range of 50 to 1000 eV was used. The ablated  $\text{B}_4\text{C}$  reached the target and reacted with nitrogen ions and formed B-C-N films. The films were analyzed by XPS and Raman spectroscopy. It was found that when nitrogen ions were incorporated, instead of B-C-N bonding, B-N and C-N bonds were formed. They did not investigate the mechanical properties and adhesion of the film to

the substrate. Probably they did not get B-C-N bonding due to different energy level of the species and nitrogen ion.

Savan et al [28] analyzed multi-layer nano-coatings of lubricating material, such as MoS<sub>2</sub>, in a matrix of a hard material, like TiN or CrN. They suggested different sources for the soft and hard materials. A cathodic arc evaporation technique was used to fabricate the ceramic nitride and a magnetron sputtering technique for the solid lubricant. They also developed hard material coatings on soft material coatings. By using a pin-on-disc tribometer, the coefficient of friction and wear properties were investigated for a pure MoS<sub>2</sub> film, a film of MoS<sub>2</sub> and titanium, and a film of MoS<sub>2</sub> and WSe<sub>2</sub>. The tests were carried out at 50% RH air. It was found that the two composite films had a lower coefficient of friction and much longer sliding lifetimes than the pure MoS<sub>2</sub> film under similar conditions. The interesting thing was that the composite coating of MoS<sub>2</sub> and Ti or WSe<sub>2</sub> withstood 30000 revolutions in friction tests. But, the tests were carried with a fixed ball diameter and applied load. They did not investigate altering these two parameters. From the foregoing, it would seem that in multi-layers coating, the first layer could be the soft material. And the co-generation of hard and soft materials coatings on cutting tools is a good technique.

Voevodin et al [29] synthesized nanocrystalline TiC/amorphous carbon (a-C) composite films by a hybrid process. A KrF excimer laser was used to ablate graphite. The polished 440C stainless steel substrates were cleaned for 15 minutes in 1 KeV Ar ion gun that raised the temperature to 50-80°C. There was no other heating or biasing during deposition. Carbon plumes were produced from graphite. The titanium plasma flux was produced by an unbalanced magnetron operating at a pressure of 0.2 Pa in an Ar

atmosphere. Both the fluxes intersected on the substrate surface. The distances between substrate and graphite and Ti targets were 150 mm. and 60 mm. The film thickness was found to be 0.5  $\mu\text{m}$ . The film was composed of 10 nm sized TiC crystallites bonded in a C matrix. Its hardness was found to be 32 GPa and it was highly plastic. The coefficient of friction was 0.2. They did not investigate the formation of nano-crystallites, in the above mentioned method. The conclusion is that the co-generation of hybrid coatings is a good technique to grow composite coatings on cutting tools. This conclusion is similar to Ren et al [27].

Kumar et al [30] deposited  $\text{CN}_x/\text{TiN}$  alternate layers coatings on a Si (100) substrate by the PLD method. The TiN film was first deposited at a temperature of 600°C. Its thickness ranged was from 100 to 500 nm. After that, the graphite target was ablated to produce a  $\text{CN}_x$  film at a nitrogen partial pressure of 50 m Torr at 150°C. They observed the bonding structure of the films by the Fourier transform infrared spectroscopy (FTIR) method. They found that the formation of  $\text{CN}_x$  phases was a low percentage. They observed that the elastic modulus of TiN was a function of displacement. It was also observed that the TiN layer increased the hardness of the substrate. The mechanism of the buffer effect in the film's properties was not described. The conclusion is that the target to substrate distance is a major function determining the elastic modulus of the films.

Lee et al [31] studied the laser deposition of  $\text{MoS}_2$  on a Fe nano-layer and compared it with the same film obtained by sputtering technique.  $\text{MoS}_2$  thin films were developed by using either Nd: YAG laser (wavelength 532 nm.) or a KrF excimer laser (wavelength 248 nm). In the first three samples, Fe films of 3 nm thickness were

deposited on a 440C stainless steel substrate. Either the thermal evaporation technique or KrF excimer laser PLD technique was used. These specimens were over-coated by a MoS<sub>2</sub> layer of 30 nm thickness. The samples were annealed at 850°C and at a pressure of 10<sup>-8</sup> Torr. Then, they were cooled to room temperature and kept at a pressure of 10<sup>-7</sup> Torr. The samples were analyzed by X-ray photoelectron spectroscopy (XPS) and backscattered-conversion electron Mossbauer spectroscopy (CEMS). It has been found that the PLD process involves congruent removal of the MoS<sub>2</sub> target but incongruent arrival at the surface. The sulfur reaches the substrate first. So, iron sulfides were formed. Mo and S species ejected by the PLD technique were more energetic than those produced by Nd: YAG laser. In this PLD process, there was a substantial reaction between the iron film and species of molybdenum and sulfur ejected by the plume. But, minimal reaction was observed for samples made by the Nd: YAG laser. The formation of defects in the films prior to annealing was not investigated. They did not describe mechanical properties of the films. The conclusion is that laser annealing of films might help improving the quality of the film.

#### Target condition

Kantor et al [32] studied the effect of target temperature on particulate formation. They used a KrF excimer laser to ablate In and Bi metals. The temperature of the substrate was varied from room temperature to the melting point of the substrate. For laser ablation of metals of low melting point, the characteristics of lateral dimension of laser-induced surface structure increases while the target temperature approaches to the melting point. They explained this phenomenon by numerical temperature calculations.

They found the reason for this increment is due to a low rate of heat effusion from the melt pool towards the bulk. This allows enough time for the surface to smoothen before re-solidifying again. They did not check the result numerically obtained with experimental measurement. From the above research, it can be concluded that raising the temperature of the target to the melting point during deposition might reduce the particulate formation.

Szorenyi et al [33] studied particulate formation by using both solid and liquid targets, and by choosing appropriate experimental conditions. Indium, tin and bismuth films were grown from respective targets. They used a KrF excimer laser of 248 nm wavelength and chamber pressure of  $5 \times 10^{-6}$  mbar. The glass substrate was kept at room temperature. In a molybdenum boat, target materials were heated to their respective melting points to get a liquid target. In the case of a solid target, they remelted the solid target in every 10 or 50 shots series to get smooth surface. For liquid target, the target was kept at temperature high enough to produce a vapor pressure well below  $10^{-6}$  m bar. The glass substrate to be coated was kept parallel to the target and at a distance of 44 mm from it. They found that the particulate number density on grown film reduced by orders of magnitude when liquid targets were used. But, they could not avoid the formation of sub-micron-size particulate. They got broader film thickness distribution when grown from molten targets. The conclusion is that liquid substrate can reduce particulate formation but produces sub-micron size particulates. Probably the better solution is to raise the substrate temperature to the melting point keeping the substrate in solid state.

Kim et al [34] studied the effect of target density during the growth of  $\text{TiO}_2$  films on Si (100) substrate. They used a Nd: YAG laser of 355 nm wavelength and 10 ns pulse

duration. The targets were cleaned with HF. The chamber pressure was initially  $10^{-6}$  Torr. The temperature of the single crystal Si substrate was varied from room temperature to 700°C. Two targets of  $\text{TiO}_2$  were used, one was much denser than the other. Oxygen was introduced to the chamber to achieve a pressure of 0.01 -1 Torr. High quality films were grown at 700°C and oxygen pressure of 0.01 Torr. From an AFM picture, they found that for a denser target, the film had smaller particulate size and was smoother. They did not investigate the effect of target density on the mechanical properties of the film grown. The conclusion is that the density of the target plays an important role on the particulate size and the surface roughness. Higher target density is better to grow good quality of coatings.

McGill et al [35] invented a method to combine coating materials with the target materials to form the target. When the target is exposed to laser radiation, the matrix material desorbs from the target and lifts the coating material. The target and substrate are oriented to each other so that the coating material can deposit on the substrate. The matrix material has the property of volatility and is less likely to adhere to the substrate. It helps to coat uniformly and over a large area. This method is helpful to large polymer coating. No use of this invention was found yet in the development of metal or metallic compound coatings.

Ermer et al [36] studied the formation of a fluorescent plume during the pulsed laser irradiation of wide band gap materials at sub-band gap photon energies. They used a KrF excimer laser of 248 nm wavelength. Arc-fused, single crystal MgO of 99.9% purity was used as target. The target was first polished with diamond paste, then ultrasonically cleaned with acetone. Prior to conducting the experiments, the sample was subjected to

20-25 laser pulses. It was believed that the combination of polishing and laser radiation treatment would minimize the variation in emission from pulse to pulse. The chamber pressure was kept at  $10^{-6}$  Pa. A vacuum compatible quartz fiber optic bundle was used to collect light from the region immediately in front of the sample. The light was directed to a spectrometer (Thermo Jarrel Ash Monospec-18) outside the chamber. A typical spectrum of the plume fluorescent was found to have fluence of  $3.4 \text{ J/cm}^2$ . These data were taken from the 30 ns to 140 ns laser pulse. The anticipation of the researchers was that the laser radiation damage would minimize the emission variation is ambiguous. But, the diamond polishing would help reducing variation during the first time laser radiation on the target.

#### Chamber environment

Coutal et al [37] developed a tin-doped indium oxide (ITO) thin film on a glass substrate. The sintered ceramic target was composed of a 90 wt.%  $\text{In}_2\text{O}_3$  and 10 wt%  $\text{SnO}_2$ . The chamber pressure was  $10^{-7}$  to  $10^{-6}$  Torr. The substrate temperature was maintained in the range of  $200^\circ\text{C}$  to  $300^\circ\text{C}$ . An ArF excimer laser of 193 nm wavelength and pulse repetition rate of 5 Hz was used. They admitted oxygen in the chamber at a partial pressure of 0 to 0.1 Torr. They found a good quality ITO layer, with high transparency and low electrical resistivity at  $250^\circ\text{C}$  at an oxygen pressure of 0.01 Torr. Oxidizing environment at this pressure improved the film crystallinity during oxide film development. The conclusion can be made that the properties of the ITO thin film were dependent on oxygen pressure, temperature, and the dopant concentration. As the use of



ITO is mainly in the field of electrical and optical, the research investigated those properties only.

Park et al [38] studied the adhesion mechanism of copper films on an alumina substrate. The substrate was 99.6% pure alumina with an initial roughness of 0.1  $\mu\text{m}$ . It was laser irradiated prior to copper deposition. The wavelength of the laser was 308 nm. The chamber atmosphere was either oxidizing (air) or reducing (an Ar – 4%, H<sub>2</sub> mixture). Their pressure was at 1 atm. Pure copper film (99.9% purity) of thickness 80 nm was deposited after irradiating the substrate by an ion-beam-sputter. The base pressure of the chamber was  $1 \times 10^{-6}$  Torr and the working pressure was  $1 \times 10^{-5}$  Torr. After that, the metallic film- alumina specimens were vacuum annealed (pressure  $5 \times 10^{-6}$  Torr) at 300°C, in some of the experiments. Copper oxides were formed on the surface of the copper films at a pressure  $5 \times 10^{-6}$  Torr. The adhesion strength was found to be a function of annealing temperature. It was also found that the high adhesion strength of copper films is due to the formation of a transitional region. When the atmosphere was air, the region was composed of two layers. The layer closer to the copper film was composed of cuprous oxide and the layer closer to alumina substrate consisted of copper-aluminum double oxide. Researchers faced difficulties to grow metal film on oxides due to the lack of adhesion. The conclusion is that, the oxidizing environment produced a transitional interface between the metal film and the oxide substrate, which helped to get a good adhesion. The discovery of a relationship between the annealing conditions and the adhesion strength was another outcome of this research. But, they could not reduce the surface roughness of the film, which was found to be about 1  $\mu\text{m}$  from peak to bottom.



Fernandez et al [39] used a magnetic field and obtained droplet-free films on six different substrates. They used a magnetic field in the axial (perpendicular to the target surface, field direction z-axis) and transverse (perpendicular to z-axis) directions. Their deposition was composed of two cylinders- one along the z-axis, (which is horizontal) and another around the vertical axis. The axial field was generated by a solenoid placed at the entrance of the horizontal cylinder. It generated 0.25 T (tesla) of magnetic field during 100 $\mu$ s. The traverse field was of 0.42 T, and was placed outside the chamber. The traverse field could be rotated. A Nd: YAG laser of 10 ns pulse duration was used. The vacuum chamber could work from  $10^{-6}$  to  $10^{-2}$  mbar. Films were grown at  $10^{-6}$  mbar. The maximum substrate temperature was 800°C. In this way, Cu films were deposited on a glass substrate and Mo films on Si. All these films were free from droplets when deposited under a magnetic field. The plume from the target might have very high energy. The impact of these species on the substrate might cause film damage, and resputtering. Majorities of those species were ions. They followed the magnetic lines to reach the substrate under a proper positioned magnetic field. The droplets mass was heavier and unaffected by the magnetic field. So, they followed a straight line from the target. It was possible to eliminate them fully. The conclusion is that the magnetic field with proper positioning works as a filter to reduce particulate in the film and produce smooth surface. And the magnetic path can guide the charged species of the plume.

Radhakrishnan [40,41] invented a method to use a free space magnetic field in the deposition chamber to get high quality thin films by diverting the ions from a plume evaporation of laser radiation of the target. He used permanent magnets to separate charged species present and neutral particulates were unaffected, and continued to pass to

the substrate. A shield allowed only charged ions curved by the magnets to deposit on the substrate. This method improves the crystallinity, uniformity and adhesion of the particulate free deposited films. The method was attempted only for a titanium carbide target and coatings on a steel substrate. The magnetic field imposed a force on the ions and deflected them orthogonal to their initial direction of travel and to the magnetic field. Neutral particles were unaffected. The advantage of this invention was that good quality film could be grown without reducing the film growth rate. The conclusion is that a magnetic field with proper positioning can improve the crystal structure, uniformity and adhesion of the coatings and can reduce or eliminate the formation of the particulates.

#### Heat treatment of the substrate

Lee et al [42] studied the growth of  $\text{PbTiO}_3$  thin films (designated as PT-PMW) onto Pt coated Si (100) substrates by the PLD method. The films were heat-treated (post annealing) after deposition. Ceramic targets, composed of  $0.9 \text{ PbTiO}_3$ - $0.1\text{Pb}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$  were prepared by conventional firing of oxides at 1000-1150 °C in a lead vapor containing atmosphere. The wavelength of the ArF excimer laser was 193 nm, and the repetition rate was 10 Hz. The substrate was coated with 200 nm of platinum. The substrate was heated by passing a dc current through itself. The substrate temperature was varied from room temperature to 650 °C. When amorphous films were grown below the crystallization temperature (<430°C), a post annealing heat treatment was conducted. By increasing the deposition temperature by 50°C every 30 minutes, to 650°C, annealing was carried out. SEM and TEM were used to study the surface morphology. The crystallographic orientation was studied by XRD. It was found that, crystallization of the

films was a function of deposition conditions, such as temperature and pressure. It was also found that phase formation in post annealing films was affected mainly by depositional oxygen pressure, rather than by depositional temperature. A different microstructure was found in the films. The deposition temperature and pressure strongly affected the grain growth and surface morphology. The problem with annealing was crack formation due to low adhesion and different coefficient of expansions of film and the substrate. To avoid this problem, the researchers suggested post annealed film deposition at a temperature of 300°C. They anticipated that it would reduce the residual thermal stress. To improve the electrical properties of the film, a control on crystallite orientation was required. But, they could not control the crystallite orientation. Probably, they would get better results if the oxygen pressure was not high during coating deposition. The conclusion is that the post deposition annealing affects the microstructure and surface morphology. The phase formation in post annealing depends mainly on the oxygen pressure for PT-PMW films.

Craciun et al [43] investigated a post deposition annealing treatment of thin  $\text{ZrO}_2$  and HAp (Hydroxyapatite) films, grown by the PLD technique. Films were deposited on a quartz or Si substrate by using a KrF excimer laser of 248 nm wavelength, 20 ns pulse duration and 5 Hz repetition rate. The atmosphere of deposition chamber was  $\text{N}_2\text{O}$ . After the films were grown, annealing was carried out below 450 °C for 1 hour and at 1 bar oxygen pressure, under very ultra violet illumination. The ultra violet radiation was produced by an excimer laser working with Xe (wavelength 172 nm). This VUV laser action produced ozone and atomic oxygen and caused oxidation reaction. They found improved optical and structural properties after completion of these two processes. At a

temperature of 600 °C or higher, annealing produced crystalline HAp layers. GIXD spectra, FTIR transmission spectra and RBS spectra analysis confirmed the high quality of ZrO<sub>2</sub> and HAp. They claimed that the lower the temperature during annealing, the better the optical properties. But, they did not give reasons for it. Probably, the surface became rough or there might be microcrack formation at high temperature, which lead to low thermal properties of the film. Annealing of HAp films, below 500°C were ineffective for crystallization and beyond 600°C lead to poor adhesion. The 100% crystalline HAp might not be a good coating because of low surface reactivity and solubility. The process of VUV treatment was not studied. The conclusion is that the lower the annealing temperature, the better the optical properties of the film.

#### Films orientation

Xu et al [44] grew epitaxial TiN thin films on Si substrates by using a KrF excimer laser of 248 nm and pulse repetition rate of 20 Hz. The system was kept at a pressure of  $2.10^{-7}$  Torr in a nitrogen atmosphere. The distance between target and substrate was 50 mm. The substrate was etched with 4.8 % HF for 10 minutes, ultrasonically cleaned for 5 minutes in acetone, 5 minutes in de-ionized water and 5 minutes in alcohol. The substrate temperature range was from 350°C to 720 °C. X-ray photoelectron spectroscopy (XPS) was used to confirm the formation of TiN by analyzing the chemical binding energy of Ti and N. They found that the orientation of the TiN thin film did not change with nitrogen gas pressure, substrate temperature, and the thickness of the film. Rather, it changed with the change of orientation of the substrate. They observed some droplets and particulate on the surface of the film. But,

they did not investigate the reason for the droplet and particulate formation. The conclusion is that the orientation of the coating depends on the orientation of the substrate.

#### Films of electrical & magnetic interest

Jia et al [45] developed smooth, particulate-free and high conductive  $\text{SrRuO}_3$  films on a  $\text{LaAlO}_3$  (100) substrate. The films were grown hetero-epitaxially at temperatures above  $650^\circ\text{C}$ . A XeCl excimer laser of wavelength 308 nm and pulse repetition rate of 10Hz was used. The oxygen pressure in the chamber was 200 m Torr. The film thickness was in the range of 100-150 nm. It was found from x-ray diffraction and a four probe test that higher temperature improves film crystallinity and conductivity. From the foregoing, it would seem that the higher temperature of the substrate determines the grain size and the microstructure of the film, which lead to lower resistivity.

Vispute et al [46] developed high crystalline quality epitaxial GaN films of 0.5 to  $1.5\ \mu\text{m}$  thickness on a  $\text{Al}_2\text{O}_3$  substrate by the PLD technique. The vacuum chamber was kept at a pressure of  $7 \times 10^{-8}$  Torr. A KrF excimer laser of wavelength of 248 nm was used to ablate a polycrystalline, stoichiometric GaN target (99.9% purity). The distance between target and sapphire (0001) substrate was kept at 7 cm. The substrate temperature was in the range of  $800^\circ\text{C}$  to  $1000^\circ\text{C}$ . The crystalline quality of the GaN was confirmed by four circle x-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS) and ion channeling. The surface morphology, optical properties and electrical resistivity were observed by atomic force microscopy (AFM). They found that the crystalline properties of these PLD GaN films were similar to those grown by metalorganic chemical

vapor deposition (MOCVD) and molecular beam epitaxy (MBE). They found a decreased growth rate with increase of substrate temperature. They also grew AlGaIn when the substrate was exposed to  $\text{NH}_3$  prior to deposition. The conclusion is that the film deposition rate decreases with the increase of the substrate temperature.

Narasimhan et al [47] studied the structural, electrical and optical properties of thin zinc oxide films deposited on a glass substrate by the PLD method. They investigated the properties of the film deposited at substrate temperatures of 300-575 K and 5N oxygen partial pressure in the chamber. They found that electrical dc resistivity was independent of substrate temperature. This result was different from that obtained by Jia et al [45] for a  $\text{SrRuO}_3$  target on a  $\text{LaAlO}_3$  (100) substrate by the PLD method. Probably the grain size, microstructure, doping of oxygen and characteristics of the material, accounted for this difference.

## Chapter III

### PROBLEM STATEMENT

The pulsed laser deposition (PLD) technique is employed to grow  $B_4C$  and  $MoS_2$  nano-coatings on cemented tungsten carbide (WC + 6% Co) cutting tools. The coating should be adhesive, wear resistance and of low surface roughness. The  $B_4C$  coatings should provide high hardness and wear resistance. The  $MoS_2$  coating should provide lubrication. Numerous alternate layers of  $B_4C$  and  $MoS_2$  nano-coatings furnish the WC substrate the hard and wear resistance property of  $B_4C$  and solid lubricating property of  $MoS_2$ . The effect of magnetic and electric field on the growth rate of  $B_4C$  nano-coating is also studied.

## Chapter IV

### APPROACH

To obtain good adhesion of the coating to the cemented tungsten carbide substrate, the surface of the tools are polished to a mirror finish, cleaned with acetone, cleaned ultrasonically, and/or etched by the Murakami technique. Before commencing the coating process, the surface of the substrate is scanned by a split laser beam. Substrate preparation was considered as an initial step in obtaining good coating adhesion.

Preliminary experiments were conducted at a substrate temperature of 400 °C to deposit the B<sub>4</sub>C coating on a WC substrate. At that time, the maximum substrate temperature of 450 °C was attainable. Optimum parameters of coating deposition were determined by the Taguchi method. A detailed description of the parameter selection is given by Raman [48] and Ravikumar [49]. In their procedures, the optimum parameters were found as follows:

The target and substrate distance = 2 cm.

Laser pulse energy = 100 mJ.

The chamber pressure =  $5 \times 10^{-5}$  Torr.

Laser frequency = 10 Hz.

The substrate temperature = 450°C,



In the later experiments, the above parameters are used except for the substrate temperature and laser energy. It has difficult to maintain 100 mJ laser energy in all experiments because the gases in the laser dissociate and thereby decreasing the laser energy.

Initially good adhesion was not found. It is believed that the substrate temperature is inadequate to achieve good adhesion between the substrate and the  $B_4C$  coatings. Thus, it is essential to increase the temperature of the substrate. So, the substrate temperature is elevated to 600 to 700 °C range. The temperature beyond 700 °C is not achievable by the present experimental set up. Even, if the substrate is kept at 700 °C for long time (about 1 hour), there is a chance of breakage of glass in viewing port. As it is difficult to maintain such a high temperature for a long time, the temperature is reduced to 400 to 450 °C range after the first 5000 to 20000 pulses. By this time, a few layers of the  $B_4C$  coating would have formed on the WC substrate. The first layers of  $B_4C$  will enjoy high temperature and should have good adhesion. The rest of the coating will grow on the initial layers of  $B_4C$ .  $MoS_2$  would grow on  $B_4C$  at lower temperature ranges, which is less than 400 °C, because  $MoS_2$  would oxidize above this temperature.

It is found from the literature review [21] that laser scanning the substrate (sputter etch) during film growth might help adhesion. So, in some experiments, the laser beam was split and 10 % of the beam was directed towards the substrate during the film growth process.

From the literature review [39], it is found that the magnetic field can direct the charged particles to the substrate. It can also reduce the surface roughness by filtering out large particles. To study the effect of a magnetic field, strong commercially available

magnets are applied outside the chamber, a little up from an imaginary line connecting the substrate and the target. Same number of magnets of the same magnetic power is applied on both side of the chamber to minimize any eddy effect.

To study the effect of electrical field, a positive dc current will be supplied to the substrate. The substrate will be electrically insulated prior to coating growth to avoid electrification of other equipment.

To test the adhesion of  $B_4C$  with the substrate, scribing the substrate will be done by a sharp edged chisel (SiC) and will be viewed under an optical microscope. To measure the thickness of the coating, a Zygo interferometer will be employed.

There are different factors influencing the growth of PLD coatings. They include beam energy, number of laser pulses per second, the distance between the substrate and target, the substrate temperature, the pressure of the chamber. Taguchi method will be employed to optimize the conditions for development of coating.

## Chapter V

### EQUIPMENT

Figure 4 shows schematically the equipment used in this research. It consists of an ArF excimer laser, optics and optical system, vacuum chamber, vacuum pump, substrate heater and holder, pressure gauge, thermocouple, target manipulator, laser beam power meter. The chamber, target manipulator, substrate heater/holder, vacuum pump are part of the deposition system. The excimer laser is a widely used gas system laser for PLD coatings. It gives output in the UV region. The coated and uncoated surfaces are observed by optical microscope and an optical interference microscope, which is a surface mapping microscope (MicroXam-100 is made by Phase Shift technology). To measure the thickness of the coating, Zygo interference microscope is used.

#### Excimer laser

Commercially available excimer lasers use ArF, KrF, XeCl, and XeF gas. They produce wavelengths in the range of 157 nm to 351 nm. The useful range of wavelength for thin film growth by PLD technique lies in the range of 200 to 400 nm. The advantage

of the excimer laser is that it produces short and intense UV pulses [3]. The excimer laser used in this research is made by Lambda Physik. The specification of the excimer laser used is given in the followings:

Type: ArF (class IV)

Wavelength: 193 nm.

Pulse energy: 400 m joules.

Maximum repetition rate: 10 Hz.

Average Power: 4 W

Pulse duration: 15 ns.

Beam dimensions: 24 x 6-12 mm<sup>2</sup>.

### Optics

For good quality film deposition, a homogeneous uniform laser beam is necessary. Poor beam quality leads to nonstoichiometric films and undesirable droplet formation. So, the optical system is a very important factor in the PLD technique. Optical elements get the laser beam from the laser output and steer and focus the beam on the target. The optical system comprises lenses, apertures, mirrors, beam splitter, and laser window.

The main purpose of lenses is to get the laser beam and focus it on the target to produce the required energy density for ablation. For this reason, spherical lenses are commonly used. But, cylindrical lenses can also be used for this work. Cylindrical lenses can be employed to change the shape of the laser beam, if required. There is a variety of

focusing lenses of different focal length and diameters commercially available. But, it is very important to consider the range of wavelengths transmitted by the lenses.

Laser mirrors are used to reflect the laser beam in the required direction. Dielectric multilayer mirrors are used in PLD to give a certain reflectance. These mirrors can even have 13 layers of high index and low index materials. This type of mirrors can give reflectivity of up to 99%. The reflectivity is wavelength dependent.

Beam splitters divide the beam into two or more separate beams. It can produce equal or unequal beams on its output. In this research, a beam splitter is used to split 10% of the beam towards the substrate to etch the substrate surface. In some experiments, the 10% beam is continued towards the substrate. It is believed that laser scanning of substrate can improve adhesion of a grown film.

Laser windows allow the laser beam to enter the chamber. It is important to clean the window after each coating to get repetitive results.

### Chamber

The deposition chamber is the most important part in a PLD system. A good design of chamber, substrate and target position and heating can save time and efficiency. Usually, a vacuum chamber contains a pumping port, gas inlet, pressure gauging and viewport. A PLD chamber must have ports for the target, substrate and laser beam. The chamber used in this research is large enough to allow a substrate to target distance of up to 5 cm. The chamber is made of stainless steel. Its volume is 1 liter. There are seven ports in it. A pressure gauge is mounted within the chamber to measure the inside gas

pressure A vacuum pump is attached to the chamber, which maintains the chamber pressure at  $5 \times 10^{-5}$  Torr.

#### Target manipulator

If the laser hits the target at a single point only, the target will be ablated and produce non-uniformity on the surface that will lead to poor quality of film. To avoid this problem, the target is rotated constantly. In this design, an annular disc shape region is ablated. In this project a disc shaped target is used and the laser beam hits the top surface. The target rotates on its axis and, at the same time, it also moves off center. So, a disc shape area is ablated and single point ablation is avoided.

For multi-layer coating, a maximum number of 4 targets can be exposed to the laser beam alternately. The time of exposure is dependent on the number of pulses a single target receives.

#### Substrate holder and heater

The substrate to be coated is held by a substrate holder. The distance between substrate and the target is kept at 2 cm as it was found to be optimum [48,49] during the coating process. A commercially available electrical resistance heater is located inside the holder to provide up to 700°C substrate temperature. The temperature of the substrate could be controlled from outside the chamber with an accuracy of  $\pm 1\%$ . A thermocouple probe is placed inside the holder, touching the back of the substrate to measure the increase substrate temperature. The substrate holder was rotated on its axis to produce uniform coating growth on the substrate.

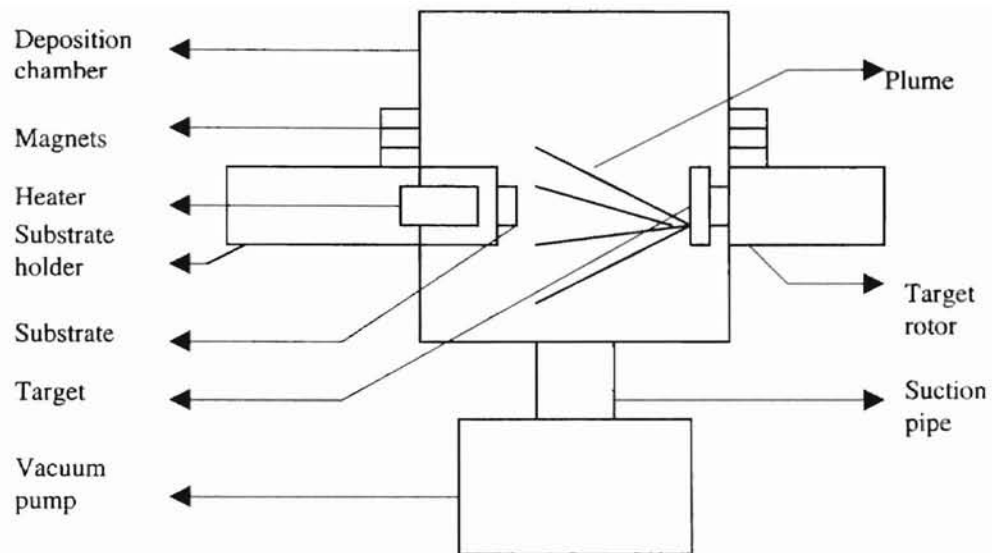


Figure 4: Front view of the deposition chamber and adjacent equipment.



Figure 5: The deposition chamber.

## Chapter VI

### EXPERIMENTAL PROCEDURE

Experiment procedure consists of the substrate preparation, coating development, testing and measurement, and safety. Experiments are initiated with the substrate preparation. The coating deposition follows. At the end of deposition, tests are carried on the deposited coatings. Safety issue is respected all along the experiments. This procedure will be discussed briefly in the followings:

#### Substrate Preparation

A  $B_4C$  target was used to provide  $B_4C$  coatings and a  $MoS_2$  target was used to provide  $MoS_2$  coatings on the same WC - 6% cobalt substrate. The square shaped substrates used were commercially available cemented WC cutting tools. For a successful coating development, substrate preparation is important. The substrate surface should be as smooth as possible and be free from all surface contaminants including any chemisorbed layers prior to any coating deposition.

The substrate was mirror polished first using diamond paste of different grit sizes from course to fine. The minimum grit size used was 3  $\mu m$ . This polished surfaced substrate was ultrasonically cleaned for 10 minutes in de-ionized water with cleaning fluid, cleaned again de-ionized water and then cleaned with acetone. This was done to



remove any physisorbed layers present on the surface. In some experiments, the substrate was used directly for deposition of coating.

In some cases, this substrate was chemically etched using the Murakami reagent. The procedure involves, the substrate treatment with Murakami's reagent (mixture of potassium hydroxide and potassium ferricyanide with distilled water in 1:1:10 ratio) for 10 minutes and then with concentrated  $H_2SO_4$  for 15-20 seconds [50]. After that, it was cleaned with de-ionized water. The objective of this etching is to remove cobalt binder present on the surface layer of the substrate. It is evident that removing cobalt binder increases adhesion. But, this process destroyed the smoothness of the surface of substrate. So, it makes it difficult to measure the coating thickness. Thus, chemical etching was not done in some of the experiments. If the Murakami reagent etches the substrate, then it is unnecessary to polish it with diamond paste before.

In some of the experiments, laser scanning was done prior to the coating deposition. This is done to clean the surface from any further contaminants. And in some experiments, 10% of the beam was split and directed towards the substrate for *in situ* cleaning. The steps used for cleaning are given in Figure 6.

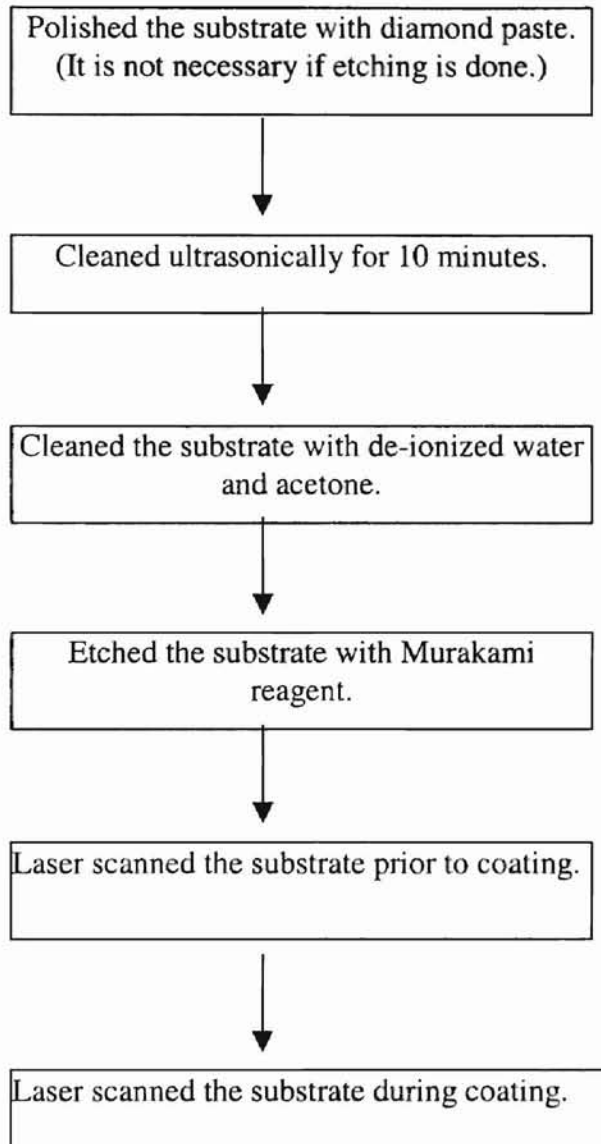


Figure 6: Substrate cleaning procedure.

### Coating Development

The chamber was cleaned prior to conducting experiments. The inner side of the chamber was first cleaned with a vacuum cleaner to collect any solid particulates. Then, it was cleaned with acetone or alcohol. It was necessary to check windows for coatings before and during the experiment. So they were cleaned, before each experiment to get repetitive results. These windows were cleaned by a special cleaner provided by Lambda Physik. Clean hand gloves were used during the cleaning operation. It is not possible to clean the windows during the development of coating. So, it was decided to observe any coating development on the front window during each experiment. Because a front window coating reduces the laser beam intensity, if the front window coatings get a dark color, the plume can not be observed. That means, the film growth process is reduced or stopped due to lack of laser energy. This is detrimental to the thin film growth process. In addition to the front window, the top window (view window) was also cleaned prior to each experiment.

Targets were abraded with silica (grade 800) to make the target surface smooth. They were then cleaned by compressed air to avoid any debris and unwanted material. An uneven target surface is not good for coating development. It increases the splashing problem, which in turn reduces the coating development rate and the quality of the thin film.

Checking the optical path is also important. The laser beam should not hit the center of the target. If it hits the center, a hollow could be formed which, in turn, will increase splashing. The split beam (10% of the laser beam) should hit the surface of the substrate.

The substrate is tightened to the substrate holder with screws, so that it will not fall down during rotation at a temperature of 700°C and vacuum. The targets are also tightened to avoid falling down.

After placing the substrate and the targets in their appropriate places, the top window is closed. It is tightened to avoid any leakage. All ports of the chamber are closed, to avoid leaks. High vacuum grease is used with the o-ring. The o-rings are changed to avoid leakage after each opening.

After closing the vacuum chamber, the vacuum pump is started. When the pressure gauge shows the designated pressure of  $(1 \text{ to } 5) \times 10^{-5}$  Torr, the substrate heater is turned on.

When the thermocouple shows the required temperature in the display, the laser is switched on and the laser action commences. The laser beam power is measured by the energy meter. For correct focusing of the laser beam and necessary beam power, the plume is seen from the top window. The target is rotated on its axis and moved laterally so that a disc shape area is ablated. When multi-targets are used, the target will change their positions after the required number of pulses. The total number of pulses is determined and is saved in the controller.

The coating will grow on the substrate during this time. To get a smooth plane coated surface, the substrate holder rotates on its axis with the substrate. The substrate temperature is monitored continuously. The temperature is maintained within  $\pm 5^\circ\text{C}$ . After coating for 5000 or 20000 pulses, the temperature is lowered to 400 to 450 °C. Because, after the first 5000 to 20000 pulses, a thin layer of  $\text{B}_4\text{C}$  will develop on the substrate. So that the next layers will be  $\text{B}_4\text{C}$  or  $\text{MoS}_2$  on  $\text{B}_4\text{C}$ . The  $\text{MoS}_2$  is sandwiched

between two layers of  $B_4C$ , in some cases. The  $MoS_2$  coating is grown at a temperature below  $400\text{ }^{\circ}C$  for reducing the chance of oxidation. At or above  $400\text{ }^{\circ}C$ , the  $MoS_2$  oxidizes with air and loses its lubricating property.

After completing the required number of laser pulses, the laser is switched off. Then, the substrate heater is turned off. When the thermocouple shows the temperature of the substrate below  $200\text{ }^{\circ}C$ , the vacuum pump is put to low vacuum position first. When the pump operates at low rpm, then it is shut down totally. The pump is not shut down when the substrate temperature is more than  $400\text{ }^{\circ}C$ . If the pump is shut down at  $400^{\circ}C$  or higher, then air from outside will enter and come in contact with the coating. It will cause rapid cooling and thermal cracking will occur on the coating. Another problem is that cooling rapidly with oxygen at high temperature is detrimental to coating adhesion with substrate.

When the substrate temperature approached to room temperature, then the top window is opened. Care is taken to avoid touching the coated sample with bare hand or breathing near it. Clean gloves and forceps are used for handling the coated sample. The samples are kept in plastic boxes to avoid any contamination. Now, these coated samples are used for analysis.

After conducting each experiment, the laser is completely shut off. The lid for the laser output is also closed. And the vacuum chamber and optical instruments are covered with plastic sheet to avoid dust deposition on them.

### Testing & Measurement

The coated surfaces were examined under an optical microscope. The surface structure and topology were observed for each sample. Uncoated surfaces were also seen at the same time to make a comparison. The power of the laser beam was measured in the optical path prior to the beam splitter.

To check the adhesion, scribing was done with a SiC tipped sharp edged chisel. The coatings with good adhesion would not peel off. The surface was observed under an optical microscope to observe the scribing mark. To measure the thickness of the nano-coatings, a Zygo interference microscope was used. A microXam was used to obtain the micrography of the topology of the surfaces of the coated and uncoated side. Surface roughness was also measured with the microXam.

### Safety & precaution

The ArF excimer laser is a class IV laser. Safety glasses were worn all the time whenever the laser is operating. Laser beam exposure to eye or skin was avoided. Federal and state laws are respected regarding safety in working with the laser. There is 5%  $F_2$  gas in the gas mixture of the laser.  $F_2$  is an extremely hazardous gas. Special attention was taken during the supply of the gas to the laser and purging the gas out.

## Chapter VII

### RESULTS & DISCUSSION

Following results are from experiments conducted in various conditions. The variable conditions are the substrate temperature, the targets, the substrate preparation procedure, presence of magnetic and electrical field. In the Table 1, all substrate preparation process was followed except laser scanning. In Table 2, laser scanning of the substrate was carried. In Table 3, a magnetic field was used. In Table 4, an electrical field was used. In Tables 5, 6, and 7 the substrate temperature was 450°C. From Table 1-5, the targets were B<sub>4</sub>C. In Table 6, the target was MoS<sub>2</sub>. In table 7, alternate layers B<sub>4</sub>C and MoS<sub>2</sub> coatings were developed.

In the following experiments (see Table 1 for details), the substrate temperature was initiated to gradual reduction to 400°C after 5000 laser pulses. It took about 20000 laser pulse time to attain 400°C temperature.

Table 1: Nano-coating of B<sub>4</sub>C on WC substrate.

Sample No.	Substrate Temperature (°C)	Energy (mJ)	Laser Pulses (x10 <sup>3</sup> )	Adhesive Coatings
1	600	78	100	Yes
2	600	76	100	Yes
3	600	140	25	Yes
4	670	140	10	Yes
5	685	126	20	Yes
6	700	140	100	Yes

In the following experiments (see Table 2 for details), the substrate temperature was initiated to gradual reduction to 400°C after 5000 laser pulses. For cleaning the substrate, 10% of the beam hit the substrate during coating. On the first and the third sample, laser scanning prior to coating deposition for 6000 pulses was done. Other cleaning procedures outlined were also carried.

Table 2: Nano-coating of B<sub>4</sub>C on WC substrate with *in situ* laser cleaning.

Sample No.	Substrate Temperature (°C)	Energy (mJ)	Pulses (x10 <sup>3</sup> )	Adhesive Coatings
1	700	104	20	Yes
2	700	102	10	Yes
3	700	95	20	Yes
4	700	154	20	Yes
5	620	152	25	Yes
6	630	150	5	Yes
7	685	145	60	Yes

Continue.



In the following experiments (see Table 3 for details), 10% of the beam hit the substrate for cleaning in sample 1 and 2. The substrate temperature was initiated to gradual reduction to 400°C after 20000 pulses. Only in the first 3 experiments, substrates were treated with Murakami re-agent. For completeness, the film thickness measurement was done by Wang.

Table 3: Nano-coating of B<sub>4</sub>C on WC substrate using a magnetic field.

Sample No.	Substrate Temperature (°C)	Laser Energy (mJ)	Laser pulses (x10 <sup>3</sup> )	Magnets on each side	Thickness (nm.)	Adhesive Coatings
1	630	100	40	1	-	Yes
2	630	92	40	1	-	Yes
3	670	88	20	1	-	Yes
4	670	82	40	1	30	Yes
5	650	80	40	2	-	Yes
6	630	150	40	3	150	Yes
7	630	120	60	3	150	Yes

Continue.

In the following experiments, a 6 volts positive dc electric charge was applied to the substrate. Complementing tests were run by Mr. Wang.

Table 4: Nano-coating of B<sub>4</sub>C on WC substrate using electric field

Substrate Temperature (°C)	Pressure (Torr)	Laser Energy (mJ)	Laser pulses (x10 <sup>3</sup> )	Thickness (nm.)	Adhesive Coatings
520	5.10 <sup>-5</sup>	120	22	-	No
550	2.10 <sup>-5</sup>	119	28	-	No

For completeness, the following experiments (Tables 5 and 6) were conducted by Mr. Ravikumar [49], Mr. Mavuleti and Mr. Zaman

Table 5: Nano-coating of B<sub>4</sub>C on WC substrate at 450°C.

Substrate Temperature (°C)	Pressure (Torr)	Laser Energy (mJ)	Laser pulses X10 <sup>3</sup>	Thickness (nm)	Adhesive Coatings
450	5.10 <sup>-5</sup>	100	100	120	No
450	5.10 <sup>-5</sup>	140	100	150	No
450	5.10 <sup>-5</sup>	150	100	150	No

Continue.

Table 6: Nano-coating of MoS<sub>2</sub> on WC substrate.

No.	Substrate Temperature (°C)	Pressure (Torr)	Laser Energy (mJ)	Laser pulses (x10 <sup>3</sup> )	Thickness (nm.)
1	450	5.10 <sup>-5</sup>	85	10	120
2	450	5.10 <sup>-5</sup>	83	15	300
3	450	5.10 <sup>-5</sup>	140	10	150

For completeness, the following experiments (Table 7) were conducted by Mr. Raman [48], Mr. Mavuleti and Mr. Zaman. Alternate layers of B<sub>4</sub>C and MoS<sub>2</sub> were coated on the WC substrate.

Table 7: Multi-layer nano-coating of B<sub>4</sub>C and MoS<sub>2</sub> on WC substrate.

Target	Cleaning Procedure	Substrate (WC) Temperature (°C)	Pressure (Torr)	Laser Energy (mJ)	Laser pulses (x10 <sup>3</sup> )	Thickness (nm.)
B <sub>4</sub> C/ MoS <sub>2</sub> / B <sub>4</sub> C	1000 pulses laser cleaning before coating.	450	5.10 <sup>-5</sup>	100	50 /10 /50	200
B <sub>4</sub> C/ MoS <sub>2</sub> / B <sub>4</sub> C/ MoS <sub>2</sub> / B <sub>4</sub> C	Chemical Etched	450	5.10 <sup>-5</sup>	100	25 /5 /25 /5 /25	150
B <sub>4</sub> C/ MoS <sub>2</sub> / B <sub>4</sub> C/ MoS <sub>2</sub> / B <sub>4</sub> C.	Ultrasonically cleaned	450	5.10 <sup>-5</sup>	100	25 /5 /25 /5 /25	225

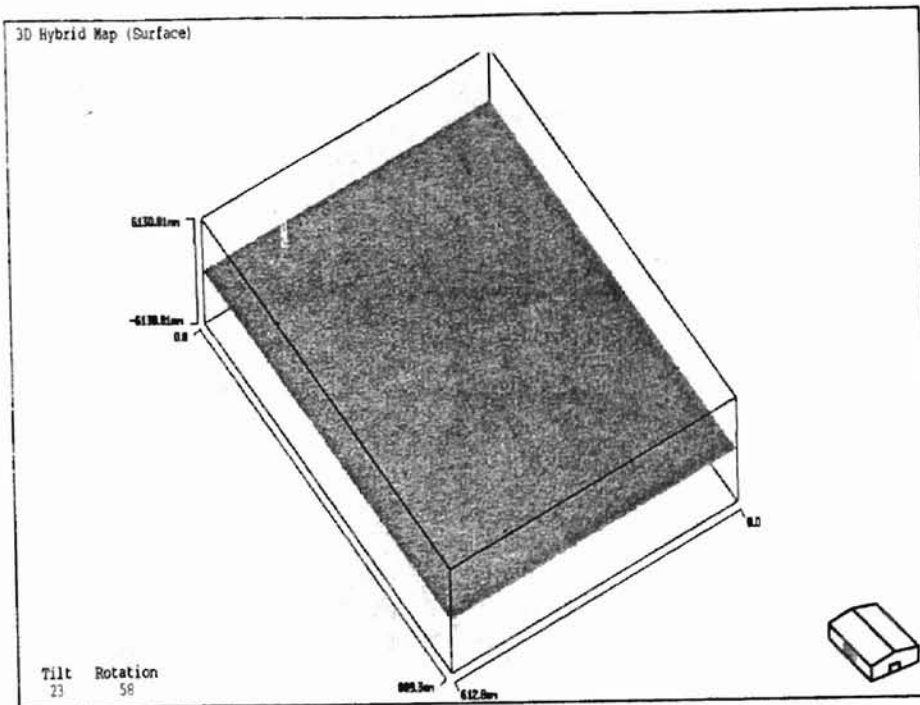


Figure 7: Three dimensional picture (sample 7, Table 3).

The Figure 7 shows a three dimensional picture showing the  $B_4C$  coated and uncoated surface of the substrate. The upper portion is the coated side and the bottom portion is the uncoated side. Between the coated and uncoated side, a step is seen, which indicates the thickness of the coating deposition. The picture was taken with a microXam at a magnification of 10.1

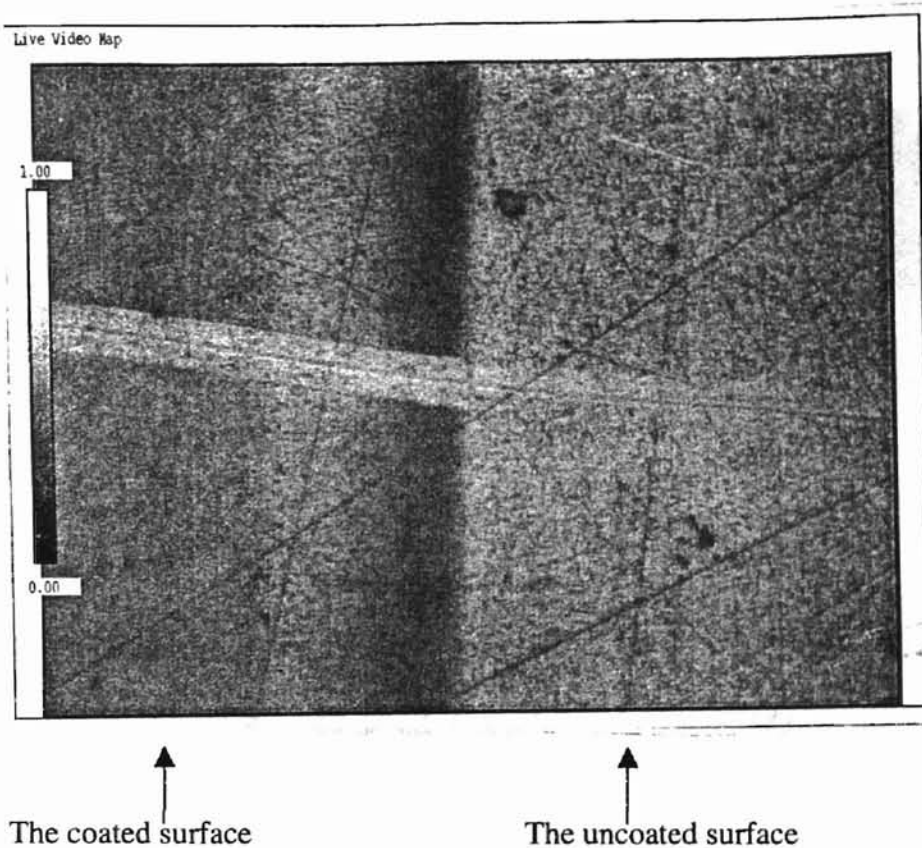


Figure 8: The coated ( $B_4C$ ) and uncoated surfaces with scribe mark (Sample 7, Table 3).

Figure 8 shows the coated and uncoated surface of the substrate. The left portion was the coated side and the right portion was the uncoated side. The scribe mark made by the chisel point is clearly visible. Some material moved perpendicular to the mark, perhaps due to the soft nature of the coatings. The picture was taken with a microXam at magnification of 10.1

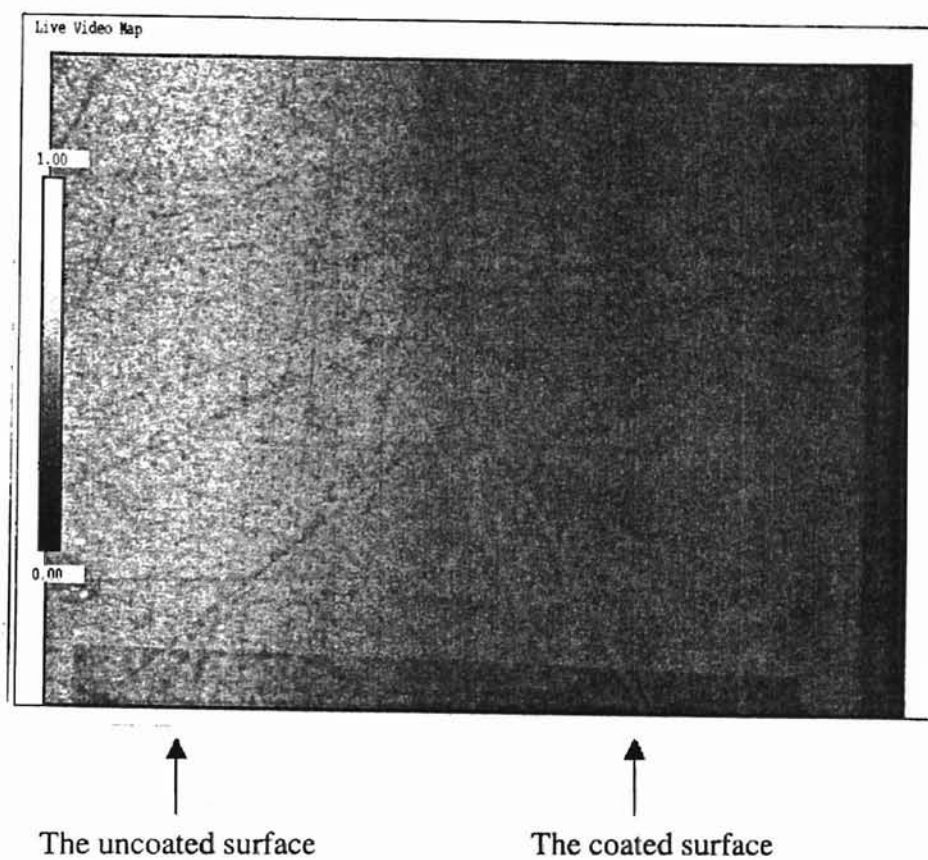


Figure 9: The coated ( $B_4C$ ) and uncoated surface (Sample 7, Table 3).

Figure 9 shows the coated and uncoated surface of the substrate. The right portion was the coated side and the left portion was the uncoated side. The color of the coated side looked dark. The surface of the coated side looked different. The picture was taken with a microXam at a magnification of 10.1

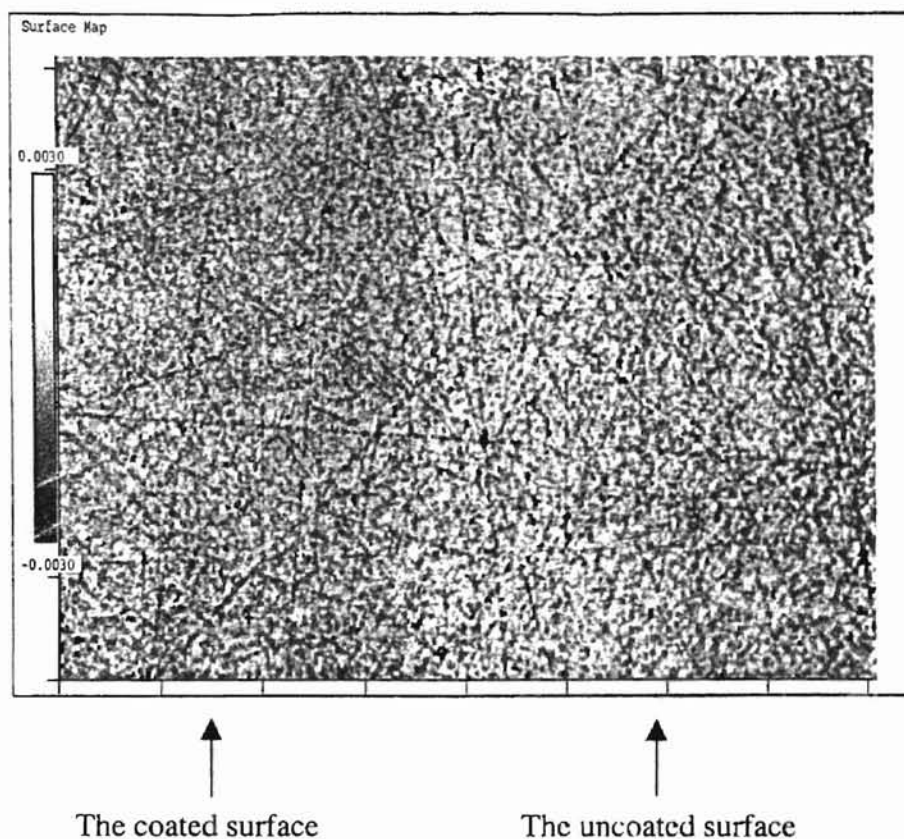


Figure 10: The surface topology of the coated and uncoated side (Sample 7, Table 3).  
Figure 10 shows the surface topology of the coated and the uncoated surface of the substrate. The left portion is the coated side and the right portion is the uncoated side. The coated side looks dark. The scratch marks are probably from the diamond polishing. The picture is taken with a microXam at a magnification of 10.1

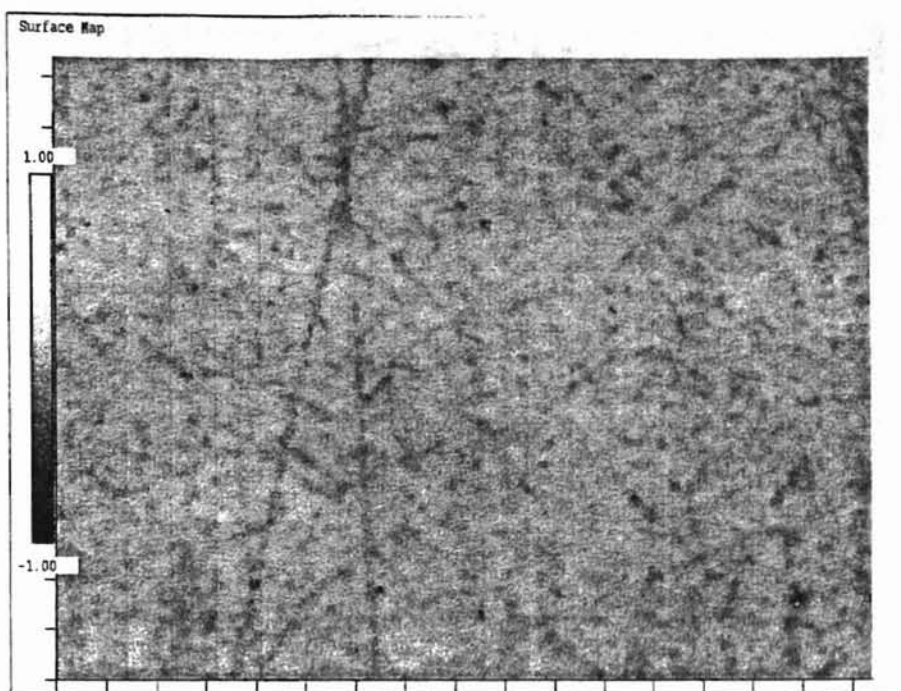


Figure 11: The uncoated surface (Sample 6, Table 3).

Figure 11 shows the uncoated surface of the substrate. The picture was taken with a microXam at a magnification of 50. The average surface roughness for this surface was found to be 33 nm.



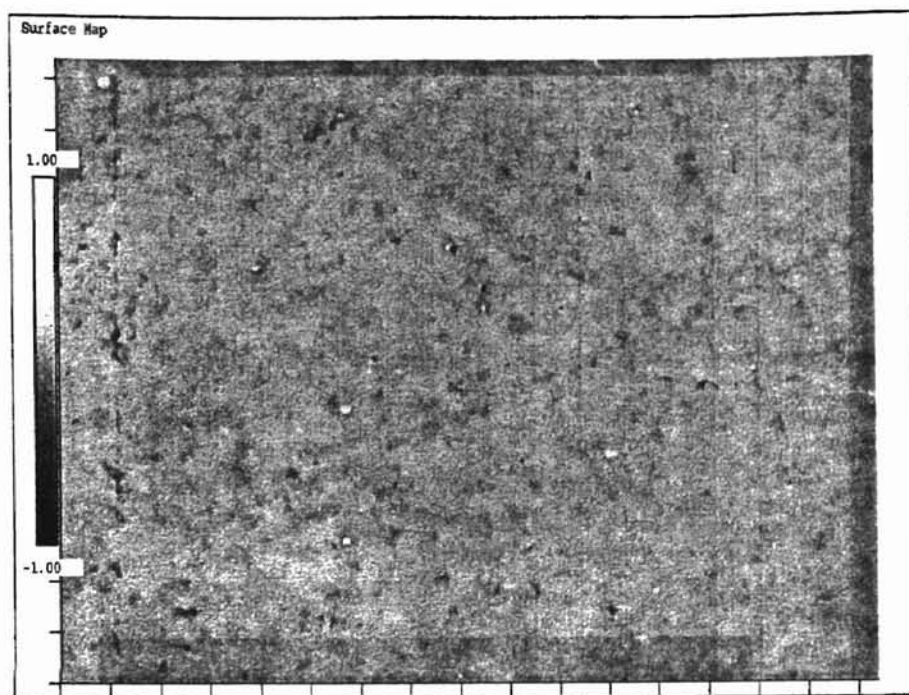


Figure 12: The coated ( $B_4C$ ) surface (Sample 6 in Table 3).

Figure 12 shows the coated surface of the substrate. The picture was taken with a microXam at a magnification of 50. Comparing this picture with Figure 10, some difference can be seen, namely the surface seemed smoother than that of the uncoated surface (Figure 10). The average surface roughness was found to be 27 nm.

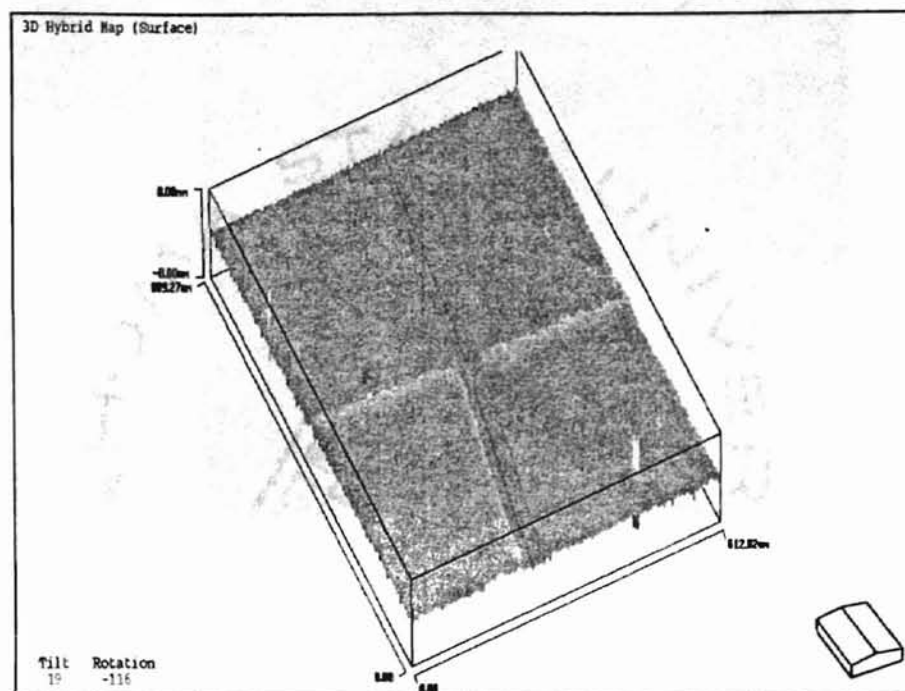


Figure 13 shows the coated ( $B_4C$ ) and uncoated surface of the substrate. The upper portion is the coated side and the bottom portion is the uncoated side. Between the coated and the uncoated side, a step is seen, which indicates the thickness of the coating deposition. The scribing mark is seen clearly on both coated and uncoated surface. The picture is taken with a microXam at a magnification of 10.1

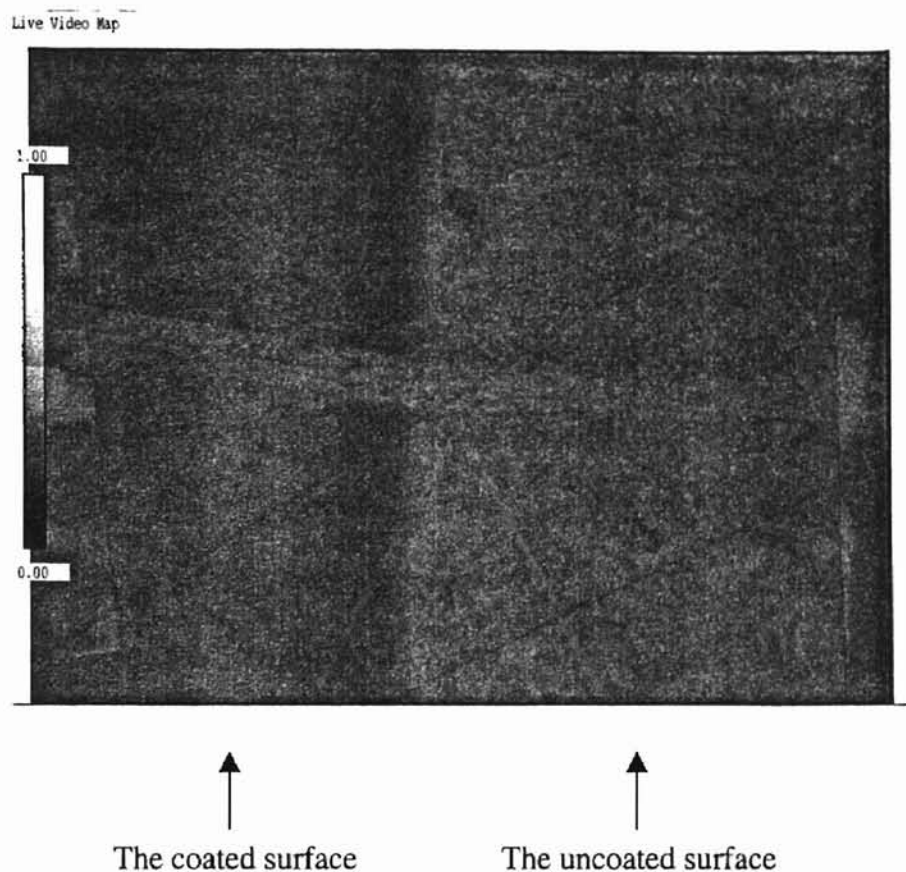


Figure 14: The coated ( $B_4C$ ) and uncoated surface with scribe mark (Sample 6, Table 3).

Figure 14 shows the coated and uncoated surface of the substrate. The left portion is the coated surface and the right portion is the uncoated surface. The scribing mark is visible on both the surfaces. The coated side looks darker. The picture is taken with a microXam at a magnification of 10.1

Observing the coated surfaces under an optical microscope, it was found that the color and the surface of the coated surface are different from those of an uncoated surface. The thickness of the coated surface was also estimated by comparing with uncoated surface. The thickness was seen as a step in some samples under the microXam. The coated surface was elevated from the uncoated surface. The coated surface was viewed to be smooth under optical microscope and the microXam (Optical interference microscope).

From the above experiments, it can be seen that the substrate temperature range of 600°C to 700°C provides better adhesion B<sub>4</sub>C coating on WC substrate than those of 450°C. The temperature range above 700°C was not investigated here. Since, it was the maximum attainable temperature with the present condition.

Laser scanning of the substrate prior to coating deposition cleaned the substrate. But its effect on adhesion was not found. As similar result was obtained by Tsui and Redman [21]. There was a difference observed between the surfaces under laser scanning during coating deposition. The surface area covered by laser scanning looked bright. But, the coated surface area without laser scanning looked dark. Oliveira et al [1] found that the color of the B<sub>x</sub>C had a relation with the number of boron (x) atoms in the compound. If the number of boron atoms were higher, then it looked dark. For lower number of boron, it was bright or less dark.

Surface roughness of the coating depends mainly on laser energy, the substrate to target distance, temperature and magnetic field. Comparing Samples 6 and 7 in Table 3, it is found that the lowering of laser energy helps to reduce the surface roughness of the

boron carbide coating. Researchers working with other coatings deposition using the PLD technique found a similar result.

Etching the substrate with Murakami reagent removed the cobalt binder and increased the surface area by making the surface rough. It was anticipated that etching with Murakami reagent might help adhesion between substrate and coating. But, its effect was not found in the experiments conducted so far.

Utilizing a magnetic field increased the coating thickness. For 1 magnet on each side of the chamber, the thickness was found to be 30 nm. For two magnets on each side, the thickness seemed thicker than that of 1 magnet, under the optical microscope. For 3 magnets on each side the thickness was found to be 150 nm. From these three observations, it was found that increasing the magnetic field causes an increase in the thickness of the coating developed.

A 150 nm thickness was found without a magnetic field when the number of pulses were 100,000 at 450°C (Sample 3 in Table 5) and laser power was 150 mJ. In Table 3, Sample 6, the same coating depth was found using 40000 laser pulses, 150 mJ laser power, 630°C substrate temperature, and three magnets in each side. The effect of temperature over the improvement of coating growth rate was found neither in the experiments conducted here nor in the literature review. Rather, it was found in literature that coating growth rate decreased with the increased substrate temperature. It was evident, that increasing the number of pulses increases the depth of coating thickness. 40000 pulses with three magnets in each side produce the same effect of 100000 laser pulses without magnetic field. Magnetic field helps to improve coating growth rate with a

lower number of pulses. So, it was found that the magnetic field increases the growth rate of B<sub>4</sub>C tremendously. But, its effect on adhesion was not found.

The effect of dc electric field could not be understood because the substrate temperature was not high enough to have adhesion. The coatings peeled off as they were not well adhesive. It was anticipated that electric field might produce similar result like that of electric field.

When the scribe mark (Table 3, Sample 6 and 7) was measured by the microXam, the depth was found to be from 1.2 nm to 100 nm in the coated surface. But the depth of the scribe in the uncoated side was found to be about 2.9 nm. The scribing was done by hand. The component of scribing force might not be the same all along. So, no conclusion can be reached from this result.

## Chapter VIII

### CONCLUSION

A study has been made on the process of development of  $B_4C$  and  $MoS_2$  nano-coatings on a WC substrate by the PLD technique. From the study, the following conclusion are made:

- The PLD is a good technique to grow  $B_4C$  and  $MoS_2$  coatings on WC cutting tools.
- The substrate temperature range of  $600^\circ C$  to  $700^\circ C$  during coating growth process gives better adhesion of  $B_4C$  coating on WC substrate than those obtained at  $450^\circ C$ .
- Simultaneous laser scanning of substrate during the coating growth process produces a bright color of the coatings. The coated surface without laser scanning has a dark color. That means either the value of  $x$  in  $B_xC$  (boron carbide) is different in these two cases, or there is a free carbon deposition. But, free carbon might come off when rubbed by a Q-tip. It did not happen. So, it is expected that the boron to carbon ratio is different.
- Magnetic field in proper positioning increases the coating deposition rate.
- Increasing the magnetic field intensity increases the coating deposition rate.

- Lowering the laser energy reduces the surface roughness of the film developed if all other parameters do not change much.
- It is possible to obtain few micrometers of multi-layers of coating of  $B_4C$  and  $MoS_2$  to improve the wear property of cutting tools.



## Chapter IX

### FUTURE WORK

It can be seen that the pulsed laser deposition (PLD) method to grow alternate hard and soft (lubricating) materials on cutting tools promises to increase the efficiency of cutting tools. To understand the process better, the followings are recommended:

The coating should be studied with atomic force microscope (AFM). Nano-indentation and/or nano-scratching test should be conducted to obtain the coefficient of friction and hardness. Because it is important, to compare the above mechanical properties with those obtained from the original coating materials.

To avoid the high substrate temperature, a suitable buffer layer/ layers can be incorporated on it, prior to coating deposition. The buffer layer can also be deposited by the PLD method. Ti, TiC or SiC may be the possible buffer layer.

Instead of  $\text{MoS}_2$ , an alternate lubricating material should be considered which could be stable at high temperatures and humid environment. ZnO may be a good choice as a lubricating material to operate at high temperatures. But, ZnO is not a good lubricant for low temperature applications. In practical cutting and tribological operations, the temperature usually raises beyond  $400^\circ\text{C}$ , if coolant is not used.

## Chapter X

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